ST ENGINEERING
LIBRARY

MAY 17 1949

JOURNAL OF

THE INSTITUTE OF PETROLEUM

FOUNDED 1913 INCORPORATED 1914

Vol. 35 JANUARY 1949 No. 301

CONTENTS

	PAGE
Integration of Operations in a Large Refinery. By K. B. Ross and D. N. McKinlay	3
A Rational Basis for the Viscosity Index System. By J. Tadayon, E. W. Hardiman, and A. H. Nissan	28
Developments in Paint Oil Extenders. By D. H. Tullis	31
The Hydrocarbon Type Composition of Cracked Gasolines. By H. C. Rampton	42
Oxidation of Turbine Oils in the Laboratory. By D. Wyllie and G. C. N. Cheesman	61
Abstracts	1A
Books Reviewed and Books Received	31A
Applications for Membership and New Members	i–ii

Published by the Institute of Petroleum.
Address: "Manson House," 26, Portland Place, London, W.1.
Telephone No.: LANgham 2250.
Telegraphic Address: Instpetech, Westdo, London.
Printed in Great Britain by Richard Clay and Company, Ltd., Bungay, Suffolk.

All rights of Publication or Translation are Reserved.

Price 7s. 6d. (Annual Subscription, £3 13s. 6d.) post free.

COUNCIL, 1948–1949

PRESIDENT:

E. A. Evans, M.I.Mech.E., F.R.I.C.

PAST-PRESIDENTS:

Sir Andrew Agnew, C.B.E.
S. J. M. Auld, O.B.E., M.C., D.Sc.
J. S. S. Brame, C.B.E., F.R.I.C.
T. Dewhurst, A.R.C.S.
A. E. Dunstan, D.Sc., F.R.I.C.
F. H. Garner, O.B.E., Ph.D., F.R.I.C.
J. Kewley, M.A., F.R.I.C.

VICE-PRESIDENTS:

E. B. Evans, Ph.D., M.Sc., F.R.I.C.
H. Hyams
V. C. Illing, M.A., F.R.S.
J. A. Oriel, C.B.E., M.C., M.A.
C. A. P. Southwell, M.C., B.Sc.
H. C. Tett, B.Sc., D.I.C.

MEMBERS OF COUNCIL:

W. S. Ault, B.A.
M. A. L. Banks, B.Sc., F.R.I.C.
A. T. Beazley, M.B.E., B.Sc., A.M.Inst.C.E.
C. T. Brunner, M.A.
E. J. Dunstan, M.Sc.
F. L. Garton, M.A., B.Sc.
T. F. Laurie
F. Morton, Ph.D., F.R.I.C.
J. S. Parker, M.A., B.Sc.
H. E. F. Pracy, B.A.
D. L. Samuel, B.Sc., A.R.I.C.
G. H. Smith, Ph.D.
E. Stokoe
E. J. Sturgess, B.Sc.
A. Beeby Thompson, O.B.E.
G. H. Thornley, M.Sc.
E. Thornton, B.Sc., F.R.I.C.
R. R. Tweed
H. de Wilde, M.Sc., M.I.Mech.E.
A. T. Wilford, B.Sc., A.R.I.C.
W. J. Wilson, F.R.I.C., A.C.G.I.

EX-OFFICIO:

Mervyn Mason, T. W. Ranson } Northern Branch.

R. B. Southall. South Wales Branch

V. Biske, B.Sc., F.R.I.C., LL.B., C. D. Brewer } Stanlow Branch.

HONORARY SECRETARY: C. Chilvers, B.Sc., F.R.I.C.

HONORARY TREASURER: G. H. Coxon

HONORARY EDITOR: F. H. Garner, O.B.E., Ph.D., F.R.I.C.

HONORARY ASSOCIATE EDITOR: E. B. Evans, Ph.D., M.Sc., F.R.I.C.

EDITOR: George Sell

GENERAL SECRETARY: D. A. Hough

TECHNICAL SECRETARY: Peter Kerr, M.A., B.Sc., F.R.I.C.

LIBRARIAN: Mrs P. Steele, A.L.A.

HON. SECRETARIES OF BRANCHES

London Branch: N. E. F. Hitchcock, c/o C. C. Wakefield & Co. Ltd., Crown Works, Hayes, Middlesex.

Northern Branch: Mervyn Mason, Matthew Walls & Co. Ltd., Bolton Street, Manchester, 3.

Scottish Branch: A. Fleming, 10 Winton Terrace, Edinburgh.

South Wales Branch: E. J. Horley, National Oil Refineries Ltd., Llandarcy, Glam.

Stanlow Branch: J. G. Hancock, "Shell" Refining & Marketing Co. Ltd., Stanlow Refinery, Ellesmere Port, Cheshire.

Trinidad Branch: J. S. Collcott, B.Sc., c/o Trinidad Petroleum Development Co. Ltd., Palo Seco, Via Siparia, Trinidad, B.W.I.

VOL. 35. NO. 301. JANUARY 1949.

THE INSTITUTE OF PETROLEUM.

AN Ordinary General Meeting of the Institute of Petroleum was held at Manson House, 26, Portland Place, London, W.1, on Thursday, October 14, 1948.

THE PRESIDENT (Mr E. A. Evans) said: I must apologize for my inability to stay for this very interesting meeting, but I have to attend another meeting. I have asked Dr E. B. Evans to occupy the Chair.

What has pleased me very much to-night is the very large audience to greet Messrs Ross and McKinlay. At first sight perhaps the title of the paper might appear somewhat uninteresting, because as soon as we hear about the integration of anything we are apt to think of a blackboard with hieroglyphics on it. But that is not the sort of thing the authors are going to discuss to-night. I am sure the meeting will be extremely interesting.

DR E. B. EVANS (Vice-President) formally occupied the Chair.

The Minutes of the preceding Ordinary General Meeting, held on June 9, 1948, were read, confirmed, and signed.

THE SECRETARY (Mr D. A. Hough) read the lists of members elected since the previous Ordinary General Meeting.

THE CHAIRMAN: The two gentlemen who are presenting the paper this evening will be very well known to most of you; both have had a very long experience in the control of refinery operations. Mr Ross, I believe, has had experience in several countries, and has been at the Abadan refinery of the Anglo-Iranian Oil Company for quite a number of years; he is the works manager of that large and important refinery. Mr McKinlay has also been associated with Abadan for a good many years and is the assistant works manager, concerned with the control of manufacturing operations.

It is quite obvious, therefore, that these two gentlemen are extremely well qualified to deal with the subject they are to discuss this evening. We are particularly fortunate to have both of them here, on leave from Abadan, to present their paper and to reply to the discussion.

MR K. B. ROSS, in presenting the paper, said: Mr Chairman and Gentlemen, at first sight the title of this paper appeared to be straightforward, but as we progressed we felt the paper had become very biased. Our knowledge of large refineries is limited to one which admittedly has the largest crude-oil throughput per day but has geographical and other peculiarities in which it differs from other refineries of comparable size. The Abadan refinery is situated on the banks of a large river, and has therefore an almost unlimited supply of fresh water. When we compare our troubles with those of the refineries which have to use seawater for cooling and have to evaporate seawater to supply feed to

the boilers, we realize what a heaven-sent blessing this geographical situation confers on the Abadan refinery.

The refinery is connected to the main oilfields by direct pipeline. I think I am correct in saying that there are very few refineries which have similar water and crude-oil systems.

In spite of these individual peculiarities we hope that, as we know no other large refineries so intimately, you will forgive us for telling you how Abadan refinery is run. We believe that the information may be of assistance to other operators, and it is always helpful to know how the other fellow tackles his job.

In addition to the detail of the numerous operations given in the paper we wish to emphasize some of the more striking features of the refinery. The stabilized crude oil from the oilfields is pumped directly into the distillation units. This allows the use of a crude oil of controlled vapour pressure, from which recovery of propane and lighter hydrocarbons for use as gaseous fuel can be effected. The percentage recovery of butane in the crude oil is kept at a high figure by the control of the vapour pressure of the crude oil fed to the refinery. Because of the *iso*butane content this ensures maximum production in the alkylation process.

The result of the use of a comparatively high-vapour-pressure crude oil and the ever-increasing inputs of crude has been to reduce crude-oil storage capacity to approximately one day's charge to the refinery. The flexibility in pumping from a number of fields and the close liaison between the Fields Production Department and the refinery has shown that this storage is sufficient to cater for emergencies.

As a matter of policy, intermediate storage of products is reduced to a minimum. In fact, in most cases, only balance storage for smoothing out production variations is used. An example of this policy is found in the case of the primary flash distillate, the 60 p.s.i. vapour-pressure cut on crude oil. Here the storage between the primary distillation and the refractionation or depropanization consists of tankage amounting to 150,000 gal capacity for a production of 1,500,000 g.p.d. This storage has proved satisfactory and adequate except in the case of one electrical failure. However, the reaction in this case, after a thorough inquiry into the occurrence, was to safeguard the position with an alternative electrical supply rather than increase the available storage. The case of kerosine is a very good example of the use of minimum intermediate storage. Here we have a sequence of operations—distillation, plumbite treating, bauxite drying, liquid-SO_2 extraction, alkali wash, and final storage—in which the intermediate storage is a total of only 4 million gal capacity of water settling between the plumbite treating and drying process for an overall production of about 1,500,000 g.p.d.

This method of operation, by which processes follow in sequence with little or no intermediate storage, can only be carried out if strict control of quality of production at each stage is maintained, and it is therefore necessary to stress the important part played by the control laboratory in providing quick and accurate testing.

The system used for the distillation of crude oil is worthy of further comment. The main system comprises a series of units consisting of a primary-pressure stage operated at 50 to 70 p.s.i., an atmospheric stage

which gives furnace-oil residue consisting of about 48 per cent by volume on crude, followed by a vacuum stage. The primary flash distillate which contains the range of hydrocarbons C_3–C_6 is fractionated in successive steps for removal of propane and recovery of mixed butanes and *iso*pentane. During the war *iso*hexane- and *iso*heptane-bearing fractions became very important as components for aviation spirits. A number of 50-, 76-, and 100-plate columns were installed to produce these substances from the primary flash distillate from the residue left after removal of *iso*pentane and the *iso*heptane cut from the atmospheric columns.

A further product from the atmospheric stage is the so-called " benzine cut." It is a fraction containing about 20 per cent of the lighter aromatics, which are extracted by a liquid SO_2 to give another component for aviation spirit.

In Abadan until the war it was considered good practice to use steam-driven pumps on cooling-water-supply duty and on such units as cracking or reforming plants where an interruption to the flowing charge might have serious consequences. However, during the war " the best laid schemes o' mice and men gang aft a-gley ", and we now have the anomalous position that cooling water to the alkylation units is supplied by electrically driven pumps. Water failures on these units can have extremely serious consequences in the release of enormous quantities of hydrocarbon vapours. Experience has now shown us that by the installation of master controllers on the steam-controlled valves by which all steam to the unit can be cut off immediately a water failure occurs, blowing of safety valves can be averted. This is quoted as an instance of how bad practices which were forced on the refineries during the war can be overcome without scrapping valuable equipment.

The part that adequate planning of maintenance overhauls plays in the integrating of operations cannot be overstressed. Units must be overhauled in the estimated time, and maintenance must be such that emergency overhauls are reduced to negligible proportions.

In conclusion, we feel that this paper could have been made very much more voluminous, but we hope that we have covered all those factors which go to make a well co-ordinated refinery and, although the recipes are all native to Abadan, we hope that in view of the increasing quantities of crude oil which are being shipped to western countries it may be a help to other refineries.

INTEGRATION OF OPERATIONS IN A LARGE REFINERY.

By K. B. Ross (Fellow) and D. N. McKinlay (Associate Member).

In this paper the methods in use in Abadan for integrating the various operations which go to make the modern large refinery are described. This refinery, judged on the crude-oil capacity (namely 500,000 barrels per day (b.d.)), is believed to be the largest in the world. The problems in co-ordinating production of a variety of products on so large a scale will no doubt be of interest to other refiners.

The refinery is situated on the Shatt-el-Arab River some 40 miles from the head of the Persian Gulf. The major portion of the products are shipped over jetties arranged along the left-hand bank of the river.

About 5 per cent of the total products are distributed to local markets by pipeline, rail- and road-tank wagon, and river and coastal craft, the remainder being exported by tanker.

Crude-oil Supplies.

The crude oil as received in Abadan is a mixture of stabilized crude from the following fields :—

Masjid-i-Suleiman
Lali
Haft Kel
Naft Safid
Gach Saran
Agha Jari.

500,000 b.d. are required for distillation in the refinery, and in addition there is the quantity required for shipment to refineries abroad. Since the storage, pumping, and distillation of the crude oil within the refinery must be carefully controlled to tie in with the deliveries from the fields a close liaison is maintained between the producing areas and the refinery through a central source in the fields. In addition, at the Masjid-i-Suleiman reservoir there are installed three topping units, the function of which is to allow an enrichment of distillate or fuel oil into the crude being despatched from that area while the unwanted material is returned to the reservoir. At one time the function of these units was of greater significance than to-day, since the effect of one million gallons per day of residue or distillate, as the case may be, was quite considerable when the total refinery throughput was of the order of 200,000 b.d. of enriched crude; to-day, however, this effect is not so apparent, since the percentage effect on the daily throughput of 500,000 brl is proportionately less. However, during the war and in subsequent years these units have provided a flexibility which has enabled the available tanker space to be used to the best purpose.

We have then before us a picture of continuous daily production of crude oil being pumped into Abadan from between 100 and 150 miles away. The crude oil is blended as required at a manifold at the entrance to the refinery and is picked up by pumps direct from the main suction lines, a boosting system maintaining the required suction pressure. Crude-oil storage tanks are located at this site and are connected to the pumping system, but the primary use of the tanks is to cater for emergency shut downs in the refinery of short duration so that there need not be a violent reduction of despatches from the fields, and in a smaller measure they provide some reserve storage. The daily pumping rate to the refinery is so high that a very large number of tanks would be required to provide an adequate reserve storage. The flexibility of the pipeline and communication systems has been demonstrated on the few occasions when it has been necessary to shut down completely, and we believe that there is no need to have large reserves of crude storage available. In addition, loss of light

ends is avoided when crude oil is pumped direct to distillation units, and the emission of obnoxious sulphuretted-hydrogen fumes from the crude is also largely avoided. By this system the use of crude oil of up to 10 p.s.i. Reid vapour pressure is possible, which provides an easy method of bringing ethane and propane into the refinery for use as fuel.

Availability of Individual Units.

After establishing uninterrupted crude-oil supplies to the refinery crude-oil feed system, the next most important factor in the integration of operations is ensuring that sufficient refining units in a good state of safety and repair are available to handle the required quantity of crude oil. This entails close liaison between the estimating, operational, survey, and maintenance groups. Forward planning of throughputs must take into consideration estimated times required for overhaul of units. The time between overhauls has been determined from data collected over a number of years, which has been correlated with existing inspection codes. The figures on pressure vessels have allowed a code to be drawn up which demands survey of pressure vessels once every 48 months. In cases of fouling of units these are not brought off service until definite evidence is available that the fouling has affected the quality of the products. By application of this code, time efficiencies are improved, resulting in more plant being available and less work being necessary by the labour force. Co-ordination of strength of labour force and work to be done is essential if high time efficiencies are to be maintained. This has only become possible in Abadan by accurate planning and progressing of all work done in overhauling units. By correct planning, emergencies, with the unplanned work associated with them, are reduced to a minimum.

Crude-oil Pumping.

Naturally the continuous pumping of the blended crude oil to the distillation units is a matter of extreme importance. The motor-driven crude-oil pumping sets, each of 57,000 b.d. capacity, total 570,000 b.d. capacity overall and are housed in three separate pumphouses, each located at a safe distance from the other to provide dispersal in case of fire. The crude-oil pumping system can therefore be regarded as safe from being completely shut down except in the case of a general power failure.

Crude-oil Distillation.

While in general it may be said that forward market demands dictate the programming of the throughput of a refinery, in actual practice to-day the world demand is for maximum production of petroleum products, and it is principally availability of refinery capacity which sets the throughput of a refinery from month to month. It has already been shown how adequate planning should ensure maximum production and the order of the priority which is accorded to the various products in demand.

Before proceeding to describe the products of crude-oil distillation their

collection and disposal, a brief enumeration of the major products required for marketing is given below. These products are :—

Aviation spirits
Motor spirits
Special boiling spirits
Kerosines
Vaporizing oils
Gas oils
Marine diesel oils
Fuel oils
Bitumen.

Size of Distillation Units.

The distillation capacity down to atmospheric residue consists of four large units each of 85,500 b.d. capacity and five units each of approximately 28,500 b.d. The original pipe-still units in the refinery were of 28,500 b.d., but in 1936 the first 85,500-b.d. unit was commissioned. With further increases of throughput, all in 85,500-b.d. steps, the loss in throughput caused by overhauling one of the large units has become less marked. With further reductions in overhaul time due to increased planning and revised inspection codes, the effect of the loss of one large unit on total throughput will be correspondingly less. The units are fully instrumented and therefore call for low operating manpower.

Operation of Distillation Units.

In order to obtain the various final products indicated above the units are operated to give the following actual fractions :—

Gas at 60 p.s.i.
Primary flash distillate containing hydrocarbons in the C_3 to C_6 range.
*Iso*heptane base containing mainly C_7 hydrocarbons.
Straight-run benzine.
Naphtha reforming cut.
Aromatic cut for solvent extraction.
Unrefined kerosine for burning oil and vaporizing oil.
Gas oils.
Atmospheric residue.

The atmospheric residue undergoes further distillation using ancillary heaters and vacuum columns to provide gas oil, waxy distillates, and bitumen.

All these products are not simultaneously derived from one individual unit, but rather from the combined output of several such units, one perhaps producing *iso*heptane base from the atmospheric column overhead, while another unit will provide from its atmospheric column overhead the required straight-run benzine. In the same way aromatic cut for solvent extraction for aviation-spirit manufacture may be produced on one distillation unit while a companion unit may, from a similar side stream, produce a virgin reforming stock.

The amount of gas liberated on distillation of 500,000 b.d. crude oil is some 18 million cu. ft. per day. Recovery of butanes and gasoline from the gas is practised, the residual gas being used for the recovery of sulphur after which it is blended into the refinery fuel-gas system. An adequate venting system to atmosphere caters for emergencies.

Production of Aviation Spirits.

The P.F.D. or primary flash distillate, which is obtained as the overhead condensate from the primary distillation (column-base pressure is 70 p.s.i.), is passed forward to a series of fractionating columns for fractionation. The first operation is carried out using high-pressure columns where propane and lighter hydrocarbons are liberated under controlled conditions to join with the gas from the primary flash equipment for H_2S recovery and subsequent use as fuel. The maintenance of continuity of operation at this point is vital, since a shut-down here would disorganize and eventually shut down the whole of the distillation process: standby capacity is essential.

The stabilized product, namely the depropanized gasoline, contains some 25 per cent of butanes. These mixed butanes are recovered in a succeeding distillation and passed forward via a mercaptan-removal unit to the alkylation process for the recovery of *iso*butane which amounts to some 20 per cent. The balance, *normal* butane, provides feedstock for the ancillary isomerization process. The provision of C_4 (about 8,550 b.d.) is the first link in the chain between crude oil and aviation-spirit production. The integration of operations whereby depropanization, debutanization, and de-*iso*pentanization are carried out in successive columns is very close and must be maintained. If the butane fractionation is lost, an escape route for the undebutanized gasoline into straight-run benzine is available, but it has its effect in shutting down plant in the back end of the aviation chain. Upon debutanization of the primary flash gasoline the product is quite stable at about 10 to 12 lb Reid vapour pressure and suitable, after treatment, for inclusion in motor spirits, but all the *iso*pentane in the crude oil is concentrated in this residual fraction.

Since *iso*pentane is included as a blending component in aviation spirit it becomes necessary for a certain proportion of this debutanized gasoline to be fractionated to provide the required amount of *iso*pentane. The quantity required is some 4,000 b.d. It is obvious, therefore, that another link between crude oil and aviation spirit exists here and the operation of depropanization and debutanization must proceed before *iso*pentane can be made available for aviation spirits. It may be remarked here that the storage for depropanized gasoline and for debutanized gasoline is practically negligible, consisting merely of balance tanks which give little more than an hour's total storage, and therefore any emergency must be taken up by provision of the necessary spare capacity. Continuity of production is therefore essential and it is obvious that behind this part of the process the treatment units must be in a position to be able to deal with the product. Failure to produce butane and *iso*pentane will not shut down the refinery, but will slow down production of aviation spirits.

After the removal of *iso*pentane the balance of the gasoline is split up. A portion, depending upon the market demands, is bled off for mercaptan removal and then included in motor spirits. The remainder is passed forward to storage tanks from which it is pumped to fractionating columns for the removal of some 5,700 b.d. of *iso*hexane concentrate.

The *iso*hexane base storage capacity is comparatively large and therefore a certain amount of latitude is possible in the integration of the passing forward of the base stock and the production of the *iso*hexane. However, loss of time can generally be ill afforded and an inordinate loss of time in the segregation process would result in having to turn away base stock which would mean a direct loss to production. By "topping" and "tailing" the *iso*hexane base a product is obtained which, after acid treatment and re-running for removal of sulphur, is used as a blending agent for 100-octane aviation spirit. The discarded materials are blended into naphtha-reforming stock.

So far we have dealt with the products of the primary distillation of the crude oil. Let us now consider the fractions in order of volatility as they are distilled from the crude oil under atmospheric pressure. First, we have the overhead product from the various atmospheric columns. This material contains most of the *iso*heptane available in the crude oil and most of it is used to provide an *iso*heptane-bearing base feedstock while the balance may be used, after sweetening, as a straight-run benzine in the blending of motor spirits.

Taking the *iso*heptane base first, this material is pumped to base feed tanks which provide a limited amount of storage. It is then fractionated in a series of 100- and 50-plate columns, the "tops" providing an additional base feedstock for *iso*hexane; the bottoms are blended with naphtha-reforming stock. The middle cut, some 7,100 b.d., is the *iso*heptane which, after treatment with 98 per cent H_2SO_4 and subsequent redistillation for removal of sulphur, is blended in 100/130 grade aviation spirit.

The remainder of the atmospheric column overhead product is refined to low-mercaptan-sulphur content and, along with cracked spirit, is used in blending motor spirits.

The first side stream from the atmospheric column is usually a product of about 0·760 sp. gr. containing about 20 per cent of aromatics which can be extracted with liquid SO_2 in an Edeleanu type of plant. The extract, after sulphur removal, has a fairly high octane number and a high rich-mixture number. Manufacture of this product demands: (1) a continuous distillation of crude oil to provide the daily amount of feedstock, (2) the liquid SO_2 extraction of some 20,000 b.d. of base, (3) acid treatment in a counter-current type of washery, (4) continuous operation of a redistillation unit to remove sulphur down to a figure as low as 0·003 per cent. All these operations employ small intermediate tanks as buffer-storage vessels, but the combined storage is quite limited, and the necessity to maintain continuous production is paramount.

Since the total amount of this particular fraction of the crude oil is more than that required for aviation-spirit base stock, the balance is continuously passed forward to mix with the discards from the *iso*heptane and *iso*hexane distillations and the raffinate from the SO_2-extraction plant to provide the required amount of reformer feedstock.

Prior to the production of aviation spirit in Abadan the use of reforming was confined mainly to the upgrading of naphtha for the production of high-octane motor spirits. The position has now changed and, within limits, it may be said that the primary purpose of reforming in Abadan is the production of butenes for the alkylation process. The cracked spirit produced from the reforming units is leaded and therefore need not be of high quality.

The amount of unsaturated C_4 which is derived from the reforming units controls the daily production of butene alkylate. Associated with the cracked spirit derived from reforming there is a pentene cut which can be fractionated out of the spirit and alkylated with *iso*butane to provide pentene alkylate. It is therefore most essential that the required reforming throughput is made available and that the complete utilization of the butenes and pentenes is accomplished by having the alkylation units available to deal with the unsaturates. With a high aviation spirit demand it is essential that alkylation capacity should not be idle for want of feedstocks. This illustrates the necessity for efficient planning to co-ordinate the operation and overhaul of reformers and alkylation units.

The manufacture of aviation spirits, both 91/98 and 100/130 grades, demands the production of *iso*pentane, *iso*hexane, *iso*heptane, benzine extract, and alkylate. We have shown the place of each component in its separate manufacturing system and its relation to the preceding and subsequent operations. A smooth integration of planning, operation, subsequent treatment, and blending is necessary if optimum production is to be achieved.

Before leaving the manufacture of aviation-spirit components an indication of the equipment in use will give an additional idea of the extent of the operations and the need for careful planning of the interdependence of units.

Alkylation capacity, consisting of three separate units, is 10,000 b.d. Associated with each alkylation unit is an isomerization unit, each of capacity 2,000 b.d. of net *iso*butane. Two anhydrous hydrochloric-acid-manufacturing plants provide the HCl for activating the aluminium-chloride catalyst in the isomerization process.

*Iso*hexane production is carried out using 1×50 plate and 2×76 plate columns. The *iso*heptane fractionators are 2×100 plate columns for the first operation, or topping process, and 2×50 plate columns for the second operation, that is removal of the *iso*heptane overhead.

A 20,000-b.d. SO_2-extraction unit provides the benzine extract of aromatics; associated with this unit there is an SO_2-production unit producing more than 2 tons sulphur dioxide per day.

Sulphuric acid for the alkylation process is manufactured in an adjacent area. Here there is also situated a plant for recovery of sulphuric acid by the destruction of sulphuric-acid sludges.

Electric power is supplied from the main power station. Water cooling is provided by three cooling towers in the area, each with a capacity equivalent to 2 million Imp. gallons per hour. The steam requirements are met from the area boiler battery with a maximum continuous rating of some 1,600,000 lb per hour. The planning of the overhauls of the utilities in the general scheme is also, therefore, a very vital necessity.

Production of Motor Spirit.

The manufacture of motor spirit to-day shows a marked difference from production prior to the war. This change has been brought about to a great degree as a result of the impingement of aviation-spirit production on the refinery manufacturing programme involving a change in the functions of various plants. In order to stress the change of importance of products for which allowance must be made in the co-ordination of processes in the refinery a brief description of pre-war motor-spirit production will not be out of place at this point. In 1938–39 motor spirits were blended according to various market demands and ranged from ordinary motor spirits to premium-grade spirits having octane numbers of 77/78. The bulk of the spirit was manufactured by blending cracked spirit of 70/72 octane with some straight-run benzine; a percentage of blending gasoline was also added to provide volatility at the front end. Depending upon the proportions of the main blending components, the refined motor spirit could be adjusted to give the required octane number, volatility, and Reid vapour pressure. Since the majority of the grades in demand necessitated no higher octane number than 72 it was possible to blend without the addition of T.E.L.

For the special grades the new polymer gasolines were added to provide the higher octane numbers. The type of plant which produced this was a plant designed to polymerize propane–propylene and butane–butylene derived from cracking-plant gases which hitherto had been burnt to waste and were now converted to high-octane gasolines for inclusion in premium-grade motor spirits. To provide the base stocks for these polymerization processes it was necessary to depropanize and debutanize the cracked distillate from the reforming process and the surplus C_4 was eventually re-injected to the cracked spirits in order to correct for Reid vapour-pressure requirements. This C_4 had high blending value and represented a contribution to the motor-spirit production while at the same time minimizing venting of waste gases.

While it is seen that the pre-war manufacture of motor spirits was comparatively simple the production depended greatly upon the throughput of the reforming units. To-day, with a balance struck between the production of aviation spirit and motor spirit, the emphasis is on the production of the butenes and pentenes necessary for alkylation production as described above, *i.e.*, there is a prerequisite of maintaining a steady production of aviation spirits. The amount of cracked spirit derived from the reforming of naphtha does not constitute the main criterion of motor-spirit production, since the general tendency to utilize T.E.L. to increase the anti-knock properties of motor spirits has led to the present-day motor spirit requiring a lower octane-rating base stock. In other words, for the same amount of reforming capacity it is possible to-day to increase crude-oil-distillation capacity and absorb the extra straight-run distillate, within limits of volatility and final boiling point, to make an increased amount of benzine mainly because of the use of T.E.L. to raise the octane number of the straight-run benzine and make it a suitable motor-spirit blending agent. The limiting factor finally is the maximum

permissible dosage of T.E.L. for particular motor spirits as set by the marketing organization.

It can be seen therefore that a large measure of flexibility is available to the refiner in integrating the needs of motor-spirit and aviation-spirit production plants. When on full crude-oil throughput it is possible to produce in Abadan some 80,000 b.d. of reforming stock, and 47,000 b.d. of straight-run benzine. In the event of the treating plants for the straight-run benzine breaking down and thereby limiting flexibility to deal with the continuous treatment of the daily production of straight-run distillate, it is possible to swing the extra material into the reforming stock for which there is fairly large storage capacity. Likewise, should the reforming capacity be temporarily reduced, it is possible to maintain full crude throughput by transferring the surplus reformer stock to the straight-run benzine fraction or temporarily to include the heavier portion in the kerosine streams.

In Abadan to-day the ordinary grade of motor spirit is made by blending straight-run benzine, gasoline, and cracked spirit which has been corrected for vapour pressure by injection of the required amount of butane. The proportions of the components with their known lead responses will determine how much T.E.L. is required to give the required octane number and the other characteristics such as front-end volatility, 90 per cent point, vapour pressure, and F.B.P.

The above describes the manufacture of ordinary grade of pool spirit. Higher octane-number premium-grade motor fuels can be easily manufactured to-day by utilizing part of the high-grade components at present used in the manufacture of aviation spirit. Much depends upon the market demands as to the amount of the various motor and aviation fuel production, but it is obvious from the above that a great flexibility can exist in the range of octane numbers of motor spirits without operating extra plant.

The reforming of naphtha is limited to the minimum required for the necessary production of butenes, provided that the resultant cracked spirit is sufficient in combination with the maximum permissible T.E.L. dosage to blend off all the straight-run motor-spirit blending fractions. The pressure distillate derived from the reformers is stabilized to remove propane–propylene, which is used as refinery fuel, and the depropanized material is further processed in order to make available the butane–butene for alkylation. Acid treatment, redistillation, and final sweetening all follow in sequence as continuous operations. The programming of overhauls for acid-treatment plants and redistillation units must be carefully linked up with all the other refinery operations or once again the failure of a remotely removed process could have serious repercussions on the general refinery programme. Spare treatment capacity is available to allow for overhauls being scheduled without interrupting the general flow.

At one time the amount of kerosine manufactured played an integral part in the production of high-grade motor spirit, since the aromatic extract produced in the SO_2-solvent extraction plants had, after redistillation and refining, a high octane number, and part of it was used in the production of high-octane motor spirit. Any breakdown in part of the kerosine treatment facilities had its repercussions on high-grade motor-spirit production.

Production of Kerosines—Burning Oils.

The atmospheric distillation products so far dealt with have been *iso*-heptane-bearing base, straight-run benzine, and the cut required for extraction of aromatics in the C_8 range. The next product in order of boiling range is the unrefined kerosine, which is derived generally from the second side stream of these columns. All the similar boiling fractions in the kerosine range are collected and pumped along a transfer main to balance storage as unrefined kerosine. This material is treated by means of sodium plumbite to doctor negativity. The plumbite treatment units, three in number, are each capable of handling 14,300 b.d., *i.e.*, 42,900 b.d. The semi-refined product is then passed via balance storage through bauxite driers to remove water so that the kerosine may enter the SO_2-extraction plants and contact the SO_2 relatively free of water in order to reduce corrosion to a minimum.

The extract containing the undesirable sulphur and aromatic materials amounts to some 15 per cent and is removed continuously. The " extract " is redistilled and various " cuts " are taken off which have high-octane value because of the high aromatic content. A large portion of this was at one time used for the production of high-octane motor spirit, but to-day the bulk of the extract distillate is utilized in the manufacture of tractor vaporizing oil. The refined kerosine amounts to 85 per cent by volume, *i.e.*, some 35,000 b.d., and is pumped away immediately to final storage for shipment.

Production of Tractor Vaporizing Oil.

With the increase in kerosine-treatment capacity it has been possible to increase the production of tractor vaporizing oil in Abadan refinery. The method of manufacture is to blend the aromatic cut derived from the distillation of SO_2 extract from kerosine along with raw kerosines of diverse boiling ranges. The blend is treated with sulphuric acid in order to reduce the sulphur content. This blend of acid-treated kerosines and aromatics is mixed with a portion of heavy cracked spirit to give the required octane number, distillation range, specific gravity, and low sulphur content necessary for the tractor engine.

From the above we see how the manufacture of kerosine for burning oil becomes involved with the blending and production of tractor vaporizing oil and how both must link in with the operation of the redistillation unit and the acid-treatment facilities to give final products of kerosine, high-grade motor spirits, and tractor vaporizing oil. To cover for shut-downs in the subsequent redistillation and acid-treatment units fairly large intermediate tankage for storage of extracts exists, but in general it may be said that the process is continuous and completely integrated with the rest of the operations in the refinery. The above has described the manufacture of any grade of kerosine, but, naturally, depending upon the grade required, the distillation range can be varied by altering the cut at the crude-oil distillation units. Kerosine can, to a limited extent, slip into the reforming stock and so into motor spirit. It can also be linked with gas oils as an increase in production of the latter can be obtained by dropping the back

ends of kerosines down the tower and absorbing them into gas oils within the limits of the specification of flash point and specific gravity of the kerosine and gas oil. A fair degree of flexibility exists here.

Gas oil for high-speed diesel engines requires no treatment and is withdrawn continuously from the distillation unit and pumped to storage in the tank farm. Production is of the order of 42,800 b.d.

Special gas oils having, in particular, lower pour points which are desirable in cold climates are produced by blending with other fractions which results in a final product with the required pour point. This is purely a matter of blending.

The residue which is withdrawn from the atmospheric columns is some 50 per cent of the throughput, *i.e.*, it is some 250,000 b.d. This material is suitable as a fuel oil, but as it contains valuable gas oil part of it is subjected to vacuum distillation. Vacuum-distillation capacity (some 71,000 b.d.) exists for processing atmospheric residue, and from it are produced extra gas oil as an overhead product, waxy distillate as a side-stream product, and bitumen from the column base. The vacuum gas oil is much heavier than atmospheric gas oil and can be blended with kerosine and atmospheric residue to give the various grades of heavy diesel oils.

The waxy distillates are blended in with the residual bitumen, the balance of atmospheric residue and cracked gas oil and residue derived from the reforming of naphtha to provide the various grades of fuel oils according to the viscosities and pour points which are the main criteria.

For some time white oils and middle distillates have been in such large demand that, in spite of enriching the crude oil with distillate at the fields by operating the topping plants and discarding the residue, there has at times been a surplus production of fuel oil. It has therefore been necessary to utilize the ultimate flexibility factor, namely the re-cycling of surplus fuel oil to the wells, since fuel-oil-storage tankage has been kept full.

Production of Bitumen.

Intimately connected with the operation of the vacuum units is the production of base stocks for the various grades of bitumen. Towards attaining the maximum production it is desirable to charge the air-rectification stills with the appropriate base stock, and it is quite possible that three different vacuum columns are required to produce the different charging stocks for the simultaneous production of three grades of bitumen. A close link exists, therefore, between the air-rectification stills and the vacuum-distillation units. The supply of solvents for cut-back-bitumen production depends on the side streams being produced from individual distillation units and the continuity of operation unless cut-back-solvent storage is available.

On the other hand, closely integrated with the bitumen-production programme is the supply of drums for packaging the various grades, and the drum-manufacturing plant programme must tie in exactly with the bitumen blowing and blending schedule. It is more than likely that simultaneous production of drums for solid and cut-back bitumen is required.

Other Products.

Among the products not mentioned hitherto are special-boiling-point spirits, including mineral turpentine. The manufacture of mineral turpentine, or white spirit, is an integrated process of distillation of the required fraction on crude oil, its treatment, and subsequent redistillation. White spirit is not listed among the major products, and there is no need to expand on the part it plays in the refinery programme as a whole although, since it occupies equipment used for other products, its place in the manufacturing programme must be set. As regards special-boiling-point products, since these are generally cuts of particular boiling ranges derived from particular refined products their manufacture is not closely linked with the general refinery programme.

Likewise the manufacture of such special petroleum chemicals as di-*iso*butylene, *cyclo*hexane, toluene, ethyl benzene, and paraxylene requires special arrangements since specialist equipment may be required and it must tie in with the ordinary refinery programme. The manufacture of di*iso*butylene, if it is not to interfere with the maximum production of alkylate, requires an increased reforming of naphtha in order to provide the extra unsaturated C_4 for polymerization. This is carried out in a special plant, and the material, after debutanization and redistillation, is despatched for shipment.

*Cyclo*hexane to a great extent disrupts aviation-spirit production in that the required fraction has to be abstracted by superfractionation from *iso*heptane, and therefore the equipment used for the processing of *iso*-heptane has to be given over for this particular operation. The production of *cyclo*hexane is not closely linked with refinery operations other than the required production of aviation spirit to meet the necessary market demands. Much the same can be said concerning the manufacture of toluene, ethyl benzene, and the xylenes.

Storage of Products.

In the final analysis the throughput of the refinery and the production of the individual grades must be controlled according to a set programme of offtake. The storage capacity available for each grade of product plays a part in determining the throughputs to be run. The tank-farm receiving, storage, and loading facilities must tie in with production rates and with arrival of tankers, and should be capable of receiving and loading some two million tons of products per month. The optimum stock holding of individual products is a matter for close liaison between the marketing organization side on the one hand and the refinery production side on the other, since acute embarrassment can ensue in the event of failure to offtake the products as foreshadowed. For instance, after employing the necessary available flexibility factors it may still be necessary to cut the refinery throughput because of congestion of one particular grade of oil. On the other hand, if offtakes are allowed to increase to such an extent that stocks of the various products are reduced to minimum levels, equal embarrassment may ensue since the production of grades of oil on such high throughputs requires time for testing and checking to ensure that nothing but satisfactory materials are delivered for shipment.

Chemicals.

Associated with the treatment of white oils is the contacting with heavy chemicals, the manufacture of which is carried out in Abadan to tie in with the refinery production programme. For instance, some 800 tons of caustic soda per month is made up into soda solution. Also the manufacture of sodium plumbite for doctor sweetening must be arranged to tie in with the treatment of kerosines and straight-run benzines. In the same way the operation of producing bleach solution by leaching imported calcium hypochlorite must proceed continuously, since this chemical is also used in final sweetening processes.

The production of sulphur from the gases in the fields area is carried on continuously, as it is in Abadan utilizing H_2S-bearing refinery gases. These processes, along with acid-recovery plants, make Abadan practically self-supporting as regards supplies of sulphur. The sulphur is used in the manufacture of sulphuric acid using modern contact plants employing vanadium-oxide catalyst, the capacity of these plants totalling some 300 tons per day. Sulphur consumption is of the order of 2000 tons per month.

Liquid-SO_2-manufacturing capacity of the order of 14 tons per day is also available to supply SO_2 for the solvent-extraction processes. Although storage exists for sulphuric acid, liquid SO_2, and other chemicals, it is quite obvious that continuous production to tie in with the refinery programme must be guaranteed.

Since the Abadan Refinery is so far from other industrial areas with a background of technical organization and assistance, adequate engineering stores for carrying spare parts must be available, and workshops must operate at a high pitch of perfection in order that all these manifold refinery operations can be interlinked without major breakdowns in order to ensure continuity of production.

Utilities.

The Abadan power station which has a generating capacity of some 80,000 kW supplies power to the refinery and the housing estates of both staff and labour. Steam is supplied to both generating sets, process plants, and water-pumping units by three boiler batteries with an installed capacity of approximately 4½ million lb per hour. This capacity allows adequate standby for cleaning and overhauling boilers and auxiliaries.

The refinery water supply is pumped from the Shatt-el-Arab river and is further augmented by four water-cooling towers giving a total water pumping capacity somewhat in excess of 25 million Imp. gal/hr. The power station has a segregated water supply which is cross-connected on to the main water system.

Compressed air at 100 p.s.i. is supplied by centrally located turbo-compressors. This supply is mainly available for driving pneumatic tools. Lower pressure supplies of air are available for manufacture of blown grades of bitumen.

The authors wish to express their thanks to the chairman and directors of the Anglo-Iranian Oil Company Ltd. for permission to publish this paper.

Discussion.

The Chairman (Dr E. B. Evans): It is not often that we have an opportunity of hearing and reading such a well-balanced account of any phase of the petroleum industry as that which our authors have given us in this paper, and it is particularly valuable to those of us who are not very closely associated with the refining side; it certainly gives us some insight into the problems with which our refining brethren have to cope.

There is a very great number of points in the paper of interest to specialists and, of course, to the more general reader. I might have commented on some of them, but I believe that quite a number of gentlemen present wish to contribute to the discussion, and I feel I would do far better to leave the detailed discussion in their hands.

Mr Jas. S. Parker: Any reference to "the largest refinery in the world" requires a clear reference to the basis of comparison. In this case it is stated to be crude-oil capacity. Capacity is not a good term for this purpose, as the rated capacity of refinery plant as a whole is generally less than the refinery manages to push through it. There can be no misunderstanding about actual crude-oil throughput. If the authors can supply this figure for Abadan the following data may be of interest to them.

The two other contestants for the title "largest refinery" are generally recognized to be the C.P.I.M. in Curacao and Lago Oil and Transport in Aruba. Both these refineries operate along similar lines to those in operation at Abadan. At the beginning of this year the actual crude-oil throughput at the C.P.I.M. refinery was stated to be 350,000 b.d., and it was stated that Lago had peaked at 435,000 b.d.

Petroleum refining, though seldom referred to as such, is a mass-production job operating on liquids instead of solids, where the term is in more general use. There is one small but important difference. The production line in the case of the mass production of solids is generally inflexible. If the bolt and nut does not arrive where wanted at the exact time wanted the production line is thrown out of gear. Refinery operations, on the other hand, possess considerable flexibility. Like the pianist they can vamp until continuity of operations is re-established. As in the case of all mass-production operations, however, careful planning ahead is a necessity.

There is, of course, another side to it besides continuity of operations. Take as an example the fluid-catalytic-cracking plant at Aruba. To illustrate a point made above, this plant has a rated capacity of 15,000 b.d. and actually processes 25,000 b.d. This plant was erected in 1941 at a cost of just over two million dollars. Its present-day cost would be about seven million. Every day's shut-down of a plant carrying a capital outlay of this magnitude costs money.

This plant is scheduled ahead for definite run duration based on previous experience and engineering inspection. It was shut down after operating a nine months' schedule. It was started up again on a fifteen-month schedule. The total number of start-ups since it was completed in 1941 were eight. Shut-down periods are calculated in hours. How is this achieved? On the processing side by careful check of previous processing

results. On the engineering side by careful estimation and inspection. Replacements for any doubtful items are on the site immediately prior to a shut-down. The overhaul is handled in blitz fashion.

A combination unit of around 10,000 b.d. capacity was shut down for overhaul. Over two hundred men were on the job, each man with a definite allotted task. This unit was on stream again within 24 hr. A large refinery scores in this respect, as it has the labour available to facilitate such operations.

The key pin of refinery flexibility is storage in the broad sense, *i.e.*, in tanks, in the ground, or in tankers. Following that comes individual plant flexibility and flexibility of all operations.

Abadan has an advantage in its underground crude-oil storage. Aruba operates lagoon tankers of 2000-ton and 4000-ton capacity. Some 6000-ton lagoon ships are coming into operation. Take 3000 tons as the average haul. Processing 60,000 tons/day requires twenty lagoon tankers per 24 hr. What comes in goes out, so six deep-sea tankers of 10,000-ton capacity are required. In other words this refinery requires to turn round about twenty-six tankers every 24 hr. It is only when one gets down to figures such as these that one grasps the picture of modern large refinery operations.

Abadan adjusts the content of its incoming crude oil in a unique manner, but in the broad outline one wonders if this may not be an indication of a certain lack of flexibility in the refinery. Is there not a possibility in the long run that, unless there is a reasonable balance in what is pumped underground, a vicious circle is set up, and the incoming crude to the topping plants becomes more and more deficient in the wanted product?

Integration of operations does not necessitate other than the bare mention given to the methods by which Abadan overcomes the necessity for shipping in its large chemical requirements. "Here there is situated a plant for the recovery of sulphuric acid by the destruction of sulphuric acid sludges." One is tempted to inquire if it works.

MR R. B. SOUTHALL: I think this is a suitable occasion on which we might congratulate both authors on the part they have played in helping Abadan through the war, and maintaining it in the state of technical efficiency which exists there at the present time. For the greater part of my working life I have been at the end of one of the very long tanker lines that stretch out from Abadan, and have found great interest in what the authors have been telling us.

The paper brings out the need for constant vigilance in planning on site. I know of no other major industry where there is the need for such ordinarily efficient supervision and where the scale of operations is so vast; that the Abadan results are what they are speaks well for the brains behind all this work.

It would be interesting to hear more of the authors' views on such matters as the control of odours, the handling of sludges and emulsions, and the disposal of acid tar. Another point which is touched on only lightly in the paper is the obvious reliance on instrumentation at all stages. The fact that the instruments do work satisfactorily is evident from the general refinery results.

A comparison of this kind of paper with one that might have been delivered before the war reveals how much progress has been made in connexion with fractionation. A paper like this before the war would have referred to cuts of a certain boiling range, and quite possibly they would have been very narrow cuts; but the authors of this paper talk of actual chemical compounds. Whilst I do not suppose they represent 100 per cent purity, I am fairly certain they represent a high degree of purity. That is a very good measure of the advance that has been made.

On reading the paper and appreciating the complexity of the refinery interdependent processes, one recalls, I think it was, George Robey's definition of life as being " One damned thing after another."

MR F. MACKLEY : Perhaps I may be allowed to say that quite obviously Abadan is in quite an unusual position in respect of storage—I take it that it has not an unlimited storage for crude oil—which has its bearing on the main problem of keeping the plants available. Abadan refinery has been built up on the basis of experience over a very long period indeed and is correspondingly experienced in planning, but I should like to ask the specific question as to the approximate percentage of total time for which the plants are available and, additionally, for what percentage of time have the plants to come off-stream for unscheduled shut-downs ? Most of us have all put scheduling systems into our own refinery operations, and we hope they will work perfectly; but undoubtedly all of us in the refining word have to confess to unscheduled shut-downs from time to time. When we in England, working with perhaps a not over-generous measure of staff, experience an unscheduled shut-down in the middle of our ordinary schedule, it is a very disturbing factor indeed. I should like to ask if the authors could give an idea of the percentages so far as Abadan is concerned.

I should like also to ask something about the organization of this planning body—its responsibilities, to whom it is responsible, and what is the general liaison between the operative side, the maintenance side, and so forth. This is a matter which I think concerns some of the major oil companies in England, which are undertaking refining in a big way. Probably in some cases their problems of integration are more complex than those mentioned in the paper because, in addition to the products which Abadan is making, they will be entering the whole business of chemical operations, so that the balance of operations must be very carefully studied, and responsibilities must be clearly defined. Perhaps Mr Ross would care to expand his remarks a little on the type of organization he has at Abadan for this purpose.

MR W. S. AULT : Like our president, I was a little intimidated by the word " integration " in the title of the paper. But before I had read halfway down the first page I was disabused; and I would like to congratulate the authors on having managed so successfully to put a quart into a pint pot. I quite appreciate that they could readily have expanded almost any one of the individual sections into a complete paper.

Many of the points I had intended to raise have been mentioned by Mr Southall and Mr Mackley; but, although I feel a little diffident about

discussing refinery operation at all, being no longer concerned directly with refineries, perhaps I may be allowed to raise one or two matters.

The first concerns standby equipment, particularly pumps and compressors. I think it is most refreshing that, in a refinery of the size of that at Abadan, those responsible have had the immense courage required to eliminate almost entirely the intermediate storage between units. That step must have required a great deal of consideration before it was taken; and now that it has been taken, it must obviously bring many advantages in its train. Mr Ross has mentioned that during the war they were forced at Abadan to instal electric pumps for what might be described as master operations, although prior to the war they would have preferred to instal steam pumps, presumably turbine-driven. I would like to ask him whether they are now reconciled to the use of electric pumps for charging-stock duties and for other duties where an unexpected failure can cause great alarm and despondency, or whether they still favour steam drives?

Another question which may interest our refinery friends is, in places where they are installing electric drives for normal use, are they installing a separate electrically driven pump on a separate circuit as standby, or are they keeping a steam-driven pump as standby? Also, it might be helpful if the authors would touch on any arrangements which have been made for the automatic taking over of duty by the standby pump.

Again, the authors imply that units are not taken off service until it becomes evident that fouling is beginning to impair the quality of the products. I wonder if I am correct in interpreting that as meaning that some reduction of thoughput, possibly some considerable reduction, is accepted before a unit is brought off-stream, provided the products are still within specification.

Another matter in which I personally would be interested is that of the arrangements made for blending the crude in the manifold shortly after its arrival in the refinery. We have gathered from Mr Ross that there is no storage-tank capacity whatever in the crude flow, the tankage which is provided being in the nature of overflow tankage into which the incoming crude can be diverted if some major trouble should occur. However, returning to the blending operation, is it carried out by the manual control of instruments regulating the rate of flow on the different lines, or are the instruments automatically linked to give some sort of ratio flow control? I should like to know in broad outline what system is used.

The last point—it is one of those apparently minor points which the authors have passed over very lightly, although it must have given rise to headaches at times—is that of attaining the necessary speed of sampling and getting the results back from the laboratory. I think that any advice they can give on the methods followed to speed up that process would be exceedingly welcome to all refiners, whatever refineries they are operating.

Dr J. W. T. Jones: We have in the paper a description of a method of control which requires an enormous amount of manpower, of human effort, fairly highly paid I should think, as well as lesser-paid manpower which is brought in during the 24 hr of the day. The alternative to this very close control is tankage; but I believe that tankage is largely a lacking asset at Abadan, so that this method of control was apparently forced upon

the operators. However, they appear to like it; it is apparently acceptable. But have comparative estimates been made of the costs of the manpower and of the tankage, to which must be added the cost of the rare shut-downs, which may be rendered worse by the very close integration involved?

MR E. J. STURGESS : The last speaker has covered to some extent a point I wished to make, and that concerns storage for finished products. The authors cover the matter, and they stress the embarrassment caused in trying to meet the offtake, the tanker, and the marketing programme. The main difficulty, of course, is one of steel shortage, in connexion with this question of the additional storage which is probably desirable. But, putting the problem of steel shortage aside, what sort of finished-products storage do the authors consider to be economical? Do they want a fortnight or three weeks' storage, or would they like a little more?

MR V. BISKE : I was very interested in the authors' remarks about the importance of laboratory control. Could they give us more information as to whether they favour one centralized laboratory, or a large number of small laboratories or test rooms on the various individual plants? Further, could they say whether the test methods used are largely conventional, or whether an attempt has been made to short-circuit these by possibly using, for instance, photo-electric colorimeters or other such automatic instruments and recorders which will give an immediate indication if any of the products were to go off specification?

MR S. DARBYSHIRE : My main interest is in the gases which presumably you have in Abadan as by-products from your cracking plants; the stress so far has been mainly on liquids, I think. The gaseous chemical field, however, is becoming more and more important, and I should be very interested if the authors could give us some indication of what happens to the gaseous products at Abadan, particularly such products as ethylene. Is it the intention to carry out ethylene oxidation, or something like that?

MR P. DOCKSEY : I should like to ask Mr Ross a question on a point which occurs at the very beginning of the paper. It is stated that the crude feed to the refinery is "stabilized crude." However, judging by information given later in the paper, particularly with regard to the production of propane, I imagine the crude could not be described as "stabilized," using that in its generally accepted sense.

With regard to the point which has been made concerning the small amount of intermediate storage which is found necessary in Abadan, it occurs to me that to some extent the explanation may be in the fact that in this very large refinery a number of plants are operating in parallel.

MR E. THORNTON : With regard to this very limited storage; how do you use it? I take it you can assume that you are more likely to get a breakdown on the refinery side than on the field side; do you keep the tankage partly filled normally, so that, if a hold-up occurs in the refinery you can still hold the crude input?

There is another matter, of a semi-serious character, which I should like

to mention. I remember an occasion in the early days, when we tried to make white spirit to a specification which seemed to have been built up without reference to whether or not the ingredients were compatible—end point, flash point, compounds boiling at 190°, and so on, all came into it! For a considerable time the rejects amounted to more than the laboratory controls could handle, and they were put aside. We experienced some astonishment, and considerable delight, at the end of the month, however, on finding that the rejects consisted of the best white spirit we had ever made! So that a little storage is handy at times!

MR P. P. GRIFFITHS: My own refinery experience has been somewhat different from that of the authors; I have not worked in any refinery so large as that at Abadan, but I have been in quite a number of smaller ones—in Mexico, in Aruba, and in Great Britain. In the old days we considered ample intermediate storage to be essential, and when during the war the Government refinery at Heysham was installed to make aviation spirit, some of us thought the amount of intermediate storage put in was too small.

At that refinery, gas oil was distilled and then high-pressure hydrogenated in two stages; afterwards the hydrogenated stock was separated at distillation units into propane, butane, hydropetrol, and recycle stock. Later processes included dehydrogenation of butane, polymerization of butylenes, and hydrogenation of dimer to *iso*octane. In the early operation of the refinery it was found that, whilst all the other units got away quite quickly, a bottle-neck was caused by the dehydrogenation section of the *iso*octane units. In those days this was a new process. The people working there had a very thin time whenever anything happened to those units, since, with limited intermediate tankage, everything else had to be slowed down or stopped in turn. However, during a period of a year, as we gradually changed various engineering materials, and so on, we found we could achieve the designed capacity and eventually get well above it. Once the refinery bottle-neck was eliminated the intermediate tankage was quite adequate.

MR W. M. CATCHPOLE: The lack of intermediate tankage has been raised prominently in the course of the discussion. But I have heard a reference from Mr Parker to the necessity for bolts and nuts to arrive at the right places at the right time in a big organization, for thereby things which arrive at the same place at the same time are joined together. From the point of view of joining operations together it does seem that the question of tankage for blending has been rather neglected at Abadan; the products have to be channelled down the different production lines from the distillation units, and it does seem to me that blending in the right proportions is an important matter. That matter is one about which, I think, some of us would like to hear more.

MR E. S. SQUIRE: It was mentioned by Mr Parker that the refining of oil is a mass-production job, and he made some comparison between the mass production of liquids and of solids. But there is one big difference to which I would refer. In the mass production of solids, if something goes

wrong, and the product is out of specification, it usually has to be scrapped, but in the case of liquids there is the possibility of correction by blending at the end of the operation. Can the authors say whether that is one of the reasons why they can do with such small intermediate tankage in the refinery at Abadan?

Another factor which has been referred to as assisting in this matter is that of a number of units operating on a specific job day by day. That is not the case in many smaller refineries, however, where certain plants have to refine more than one product; at these refineries the operators are concerned with building up stocks for batching through these plants, and this accounts for the relatively large amount of intermediate tankage.

MR J. S. PARKER: Reference has been made to costs; and there is one point which occurs to me concerning the synchronization of operations. If products are run down from any refinery plant into intermediate storage, there is a loss of some of the heat which is in the oil. I am wondering whether at Abadan there is synchronization, so that products can be run from one plant to another without loss of heat. Do you do that?

DR H. M. DAVIES: I should like to carry a little further this question of parallel production and storage. Most factories in which the mass production of solid articles takes place employ nowadays the technique of control charts for controlling the quality of the manufactured products. We all know that refineries have control laboratories. The importance of these control laboratories has been stressed particularly to-night because of the fact that at Abadan the intermediate storage is cut to the minimum.

I should like to ask the specific question whether the control-chart technique, using statistical methods for fixing appropriate limits, is employed at Abadan, to cover either the quality of the products or the costs of particular operations?

MR O. A. BELL (written contribution): The authors mention that six crude-oil types are processed at Abadan refinery. It would appear to me that the operations at Abadan, the system of integration, and above all, the small amount of intermediate tankage in relation to throughput in that tankage, which was emphasized by the authors in the presentation of the paper, are all fundamentally related to the question of crude-oil feed stock.

The variation in crude-oil quality from the six fields mentioned in their paper is small as compared with that experienced in the U.S.A. or Rumania, where crudes received into the refinery may vary widely and weekly both in relation to type (*i.e.*, whether naphthenic, asphaltic, or paraffinic) and also in respect to the yields of the different products obtained from the crude oil. The former factor makes it necessary to segregate crudes for processing according to type. The second factor makes it necessary to assay *each* crude-oil tank before processing. In these circumstances it is necessary to have one tank for filling, one for analysis or assay, and the other for processing for each crude-oil unit.

I would mention a further factor in crude-oil quality, *i.e.*, emulsions, more particularly those associated with salt water. The authors state the

advantages, including the minimum of crude-oil tankage, of pumping the crude under pressure directly from the fields to the crude-distillation units. This is not possible if the crude needs treatment for reduction of water and salt content either by chemical or electrolytic desalting processes. In addition, even when such demulsification processes have been carried out, it is necessary to incorporate crude-oil settlers between the crude-oil tank and the furnace. It is evident that Middle East crudes have an exceptional advantage in this respect as compared with crudes from other producing areas.

Mr G. Vivian Davies (written contribution): In the preparation of schemes of planned maintenance I have found that a carefully drawn up plant-record system in card-index form, coupled with regular maintenance reports on various items of equipment, have proved invaluable. In the first place, it provides the basis on which to depreciate various items of plant. Secondly, it enables the age, performance, and present condition of any item of plant to be ascertained at a glance, in some suitable central office. This is also very valuable when a decision has to be made between competitive items of plant. Lastly, it provides a basis for standardization.

I would like to ask Mr Ross what type of plant record is in use at Abadan, whether such records are kept both locally and in a central engineering department, what form the maintenance report takes, and whether any standard times have been worked out for routine maintenance operations. This latter may, of course, be impossible with native labour.

Lastly, I would like to ask Mr Ross whether any degree of standardization of various items of equipment has been achieved, so that in the event of a breakdown of a complete unit, such as a pump, or part thereof, a service unit can be substituted quickly. I have found that although standardization is a long and tedious process it does yield dividends, particularly as regards electrical equipment such as motors, etc.

Mr Ross (replying to the discussion) said: I think that the correct way in which to judge the capacity of a refinery is on the basis of crude-oil throughput; but there are objections to that. Another basis that might be adopted is that of the amount of distillate produced and reprocessed. For instance, a refinery with a throughput the same as that of Abadan, but which did not manufacture aviation spirit, could not be said to be of the same "capacity." Our statement that Abadan is the largest refinery in the world, however, is based on the fact that the distillation capacity for crude oil is 500,000 b.p.d. Two years ago when I was at Aruba I was able in the course of a friendly discussion to establish with the refinery people there that Abadan is the largest refinery in the world.

I agree with Mr Parker that the normal refinery always has some flexibility in its operations. In so far, however, as shortage of intermediate tankage is concerned which limits flexibility, we had a case recently when our small primary flash distillate storage caused us considerable inconvenience. One of the distillate electric pumps developed trouble in the switchgear and the switchgear bank for all the pumps was affected with the result that the pumphouse was completely shut down. Before the trouble was straightened out we were forced to reduce the crude-oil throughput

considerably, since the primary flash distillate tanks were almost full. As part of the repercussions it was necessary, as a safety measure, to reduce the despatches of crude oil from the fields, since our crude-oil tankage had also become rather full for safe operating conditions as, at the rate of despatch of crude oil, the receiving tanks were filling very rapidly.

Although generally the refinery has flexibility, this was a case in point where rather drastic action had to be taken since there was no alternative method for dealing with primary flash distillate being produced at the high rate.

The description of the catalytic-cracking plant overhaul with the schedule prepared ahead is what all refineries aim at in these days, namely, good planning. I know that the Aruba planning system is highly developed; I am afraid that ours has not been developed to the same pitch, but we are hoping to raise it higher.

Mr Parker has expressed doubt regarding the nature of crude delivery to Abadan, fearing that the effects of recycling fuel oils would be noticed in the quality of the crude being lifted from the reservoir. This is adequately dealt with by our Fields Production Department, who take care that the recycled products are pumped into particular wells in one particular field. It should be emphasized also that at least 90 per cent of the crude oil comes from fields which have no possible contamination with recycled products, and it is from these that export shipments are made. The effect on the refinery, it can be said, is negligible.

Mr Parker also made a point concerning the supply of chemicals to Abadan refinery; other large refineries have not the same problem to the same extent. Aruba, for instance, is near enough to America to have 40 per cent caustic soda shipped in bulk by tankers. I believe also that in Curacao, sulphuric acid was shipped across from Aruba by tanker. With regard to the inquiry if the Abadan plant for the recovery of sulphuric acid works, we feel sure that Mr Parker knows of the difficulties which beset those who try to recover sulphuric acid from acid tars. However, we are making a valiant effort; in our first year we achieved 40 per cent, and we hope we shall effect improvements to increase this time efficiency. When the sulphuric-acid-recovery plant breaks down, as it does fairly frequently, we burn the acid tar under boilers in the various boiler batteries. At one time we dumped it in a hole, but the mess and smell were so great that we had to resort to burning the product.

The statement about the laboratory control has aroused more discussion than I had expected. In our distillation units, which constitute the basic process, we are extremely well instrumented and we do not seem to experience so much variation in product from hour to hour or as between four-hourly periods of test as seems to be the case in other refineries.

On our refining units we have also four-hourly tests for acidity of the final product, and we do not appear to encounter much difficulty. On the more complex units, such as alkylation units and SO_2-extraction units, we have small laboratories where there is one chemist on duty throughout each shift to test the products. In the refining area we have instituted a local laboratory; the products from the distillation side are all sent to the central laboratory for testing. Thus in principle we find that decentralization of laboratory testing is desirable and effective.

The question of the organization of the inspection and maintenance to tie in with processing was raised by Mr Mackley. We have instituted a Planning Department to deal with this side of the operations. First of all, the Planning Department start with the knowledge of the number of men who will be available during the next year and the number of overhauls that are considered necessary over that period. Our planning programme takes care of the succeeding three months in particular and the yearly programme in general. We endeavour to have the programme divided into three-monthly periods but it is not essential to run strictly to a rigid programme. A measure of flexibility is allowed so long as a plant is down for overhaul within the three months. The Estimating and Production Departments use the plan to calculate the refinery throughput and manufacture of products for the succeeding three months. Our planning is still in its infancy, but we are progressing from planning overhauls to include planning pump maintenance in order to avoid pumps being unnecessarily dismantled. We hope that by these means we shall adequately cover the maintenance of standby pumps so that we may have a guarantee that the standby pump is really in operable condition when required.

The time efficiencies of the main process plants are about 85 per cent on the crude-distillation units and 75 per cent on the reforming units. It is expected that, as a result of the new inspection code whereby periodic inspections are made at four-yearly intervals, the time efficiencies on the distillation units will be raised. The figure of 75 per cent for the reforming units may appear rather low compared with standards elsewhere, but for some years now the throughput of these units has been governed by the production requirements of unsaturated C_4 and C_5; it has not been wholly necessary to operate to the highest possible time efficiency. In the event of octane-number requirements of motor spirit being increased it will be necessary to seek higher time efficiencies from the reforming units in order to blend off the straight-run motor-spirit material.

In so far as tolerating a decreased throughput on crude distillation units as a result of fouling we allow a maximum reduction of 10 per cent of throughput on a particular unit until it can be brought into the overhaul plan.

We have been asked if we are reconciled to the use of electrically driven pumps for master operation. The evidence in our possession shows that it is satisfactory, but as operators we do not think we can state that we are altogether happy about it. We feel that this is the general view of refiners. However, the case I mentioned showed that it was possible to improve on the occasional unreliability of the electric motor by making use of instrumentation to operate controls which avoided the hazard normally brought about by using electrically driven pumps.

The broad outline of the arrangements for blending the various crude oils is that the incoming main crude-oil lines join at a manifold at the entrance to the refinery and are blended there. A particular crude may be segregated for direct delivery to a particular series of benches, while the balance of blended crude oil goes into a ring main round the distillation units. There is no control of blending by instrumentation. The quantities being delivered from each field are measured, and the simple mixing in a manifold provides all the blending necessary.

I think the point raised by Dr Jones concerning the costs of controlling quality of products *vis-à-vis* the cost of extra tankage has been answered by my remark that this method does not appear to us to be so serious as he and many others consider it. We do not find the cost excessive.

In reply to Mr Sturgess we would say that we did not mention particulars of our storage for finished products because we felt that it was a matter which was peculiar to the Abadan refinery, situated as it is, so far from the main distribution centres. The " bunched " arrival of tankers demands high stocks to prevent delays in shipment and likewise non-arrival or delayed arrival of ships requires adequate tankage to take care of production during the period of very low offtake. Our storage for black oils is equivalent to six weeks production and eight weeks for white oils. We feel, however, that this cannot be used as a guide for other refineries.

The answer to the question on the use of any type of special instruments for the control of quality of products is in the negative. pH indicators are used on the cooling-water side of alkylation units to check that leaks are not occurring which might allow hydrochloric acid to acidify the cooling water and cause corrosion.

With regard to the utilization of gases from our cracking units, we use only the butenes and the pentenes as feed stock for our alkylation units. The C_2 and C_3 fractionators are at present combined to augment the supply of gaseous fuel.

I feel that the question " What is a reasonable size of a refinery? " would lead to a great deal of discussion. Personally, I think a 10 million tons refinery is a reasonably sized unit, but I would emphasize that this is a personal opinion, since I hold the view that it is entirely a matter of the size of refinery with which a single management could handle.

Mr Docksey is quite right in his criticism of the term " stabilized crude." By stabilized crude we do not mean that the crude has been processed through stabilizers in the generally accepted sense. Crude oil for process, as well as for shipment abroad, is processed through multi-stage separators and thereby retains the useful light hydrocarbon fractions.

I agree also that the comparatively large number of crude-distillation units running in parallel enables fluctuations in quality to be smoothed out in the overall blend of any particular product. Although several crude-distillation units may have their respective side stream combined to give the quantity and quality required yet, from some distillation units, we do demand individual side streams for specific purposes to be of constant quality. We believe that our instrumentation and laboratory control do enable this to be carried out with the minimum amount of tankage. I think that this will also answer Mr Squire regarding fluctuations or errors in production of certain grades.

In reply to Mr Thornton the crude-oil tanks are operated at the half-full mark so that, in the event of an emergency arising in the refinery demanding a reduction in the throughput, we have time to communicate with our colleagues in the fields areas and to have the crude-oil despatches reduced accordingly.

As to the control-chart technique, we do not use anything like that at all in any of our operations.

In reply to Mr Catchpole we would say that with the increased through-

put of the refinery certain of the blending arrangements have not grown in proportion, but they are adequate; however, we aim to improve them in order to increase their efficiency.

The authors, in reply to Mr O. A. Bell's written contribution, entirely agree with his views. It is quite correct to say that the variation in quality from each producing field in Iran is very small, and this enables blending in a manifold to be carried out as it is. The absence of water and salt content in Iranian crude oil makes it possible to use the reservoirs as equivalent to underground storage.

In reply to a written question by Mr G. Vivian Davies, the authors' reply as follows :—

In Abadan the Inspection Department is responsible for keeping up-to-date records of all vessels, tubulars, furnace tubes, etc. A card-index system is used, and at each inspection details are entered in the appropriate record card of the condition of each individual item of plant inspected together with information on repairs and/or modifications carried out. By this means wear rates are calculated and the probable life of various plant items predicted so that overhauls can be planned in detail and the maximum use made of such time-saving devices as prefabrication.

These records are kept locally, but ultimately duplicates will be available in our London Office.

Maintenance reports are standardized for all overhauls, and include a graph showing the planned and actual times taken for the overhaul on a percentage basis, repair list, manpower used, supervision employed, deviation from plan, technical report on the work done and minutes of post-overhaul meeting held to discuss the performance of the overhaul crews.

Standardization is practised as far as possible on plant items such as pumps, motor compressors, turbines, tubulars, acid eggs, balance tanks, etc., and we are steadily moving more and more towards standardization as a real labour- and cost-cutting device.

THE CHAIRMAN : How fortunate we are in having had this paper presented to us has been very well proved by the large number who have attended this meeting, and has been even more amply demonstrated by the keenness of the discussion. I feel there may be quite a number of others who would like to join in, and I would like to emphasize that written contributions to the discussion will be very welcome; I am sure that Mr Ross and Mr McKinlay will reply to those in as excellent a manner as they have replied verbally to the discussion at this meeting.

Many interesting points have been brought out during the discussion, and it is particularly evident that, in looking after a modern refinery, with its enormous throughput and the large variety of products which have to be made to close specifications, a tremendous amount of knowledge, care, and almost superhuman wisdom is required on the part of the refinery management. Mr Ross and Mr McKinlay must certainly possess such qualities. We are very grateful to them for the amount of time and effort they have devoted to the paper, giving us the results of many years of their experience, and I ask you all to show appreciation to both these gentlemen.

(The vote of thanks was carried with enthusiasm.)

The meeting then closed.

A RATIONAL BASIS FOR THE VISCOSITY INDEX SYSTEM. PART II.

By J. Tadayon (Assoc. Fellow), E. W. Hardiman, B.Sc. (Member), and Alfred H. Nissan (Fellow).

In Part I of this paper [1] the development of the viscosity index (V.I.) system was reviewed, and three limitations of the Dean and Davis V.I. were enumerated. These were: first, above a V.I. of 140 the system was ambiguous; secondly, the V.I. is calculated from the viscosity values at two set temperatures of 100° and 210° F; thirdly, the V.I. was based on arbitrarily chosen values for hypothetical oils which were not of the same quality throughout the range of the V.I. scale. The first and third limitations were removed by evolving a formula, in which an index was correlated with the V.I. over the major portion of the scale where

$$n = \frac{\log v_1 - 0{\cdot}4336}{\log v_2}$$

v_1 = viscosity of oil at 100° F, cs.

v_2 = viscosity of oil at 210° F. cs.

It was found that n was satisfactory in characterizing an oil without ambiguity and since n is calculated by a single-function formula to be applied to all oils, there could be no break in the curves as there was with the Dean and Davis V.I. systems when v_2 was less than 8 cs. Further n was correlated with V.I. by

$$\text{V.I.} = (60{\cdot}0 - \text{antilog } n) \times 3{\cdot}63.$$

The correlation cannot be exact, nor can it apply to the full scale of the V.I., since the latter is arbitrarily chosen in certain parts of the scale whilst n follows a single mathematically controlled path.

The second limitation still remained in that n, like the V.I., was to be calculated from the viscosities at two sets of temperatures, *i.e.*, 100° and 210° F. Lapitzky [2] has shown interest in the possibilities of using the "rational viscosity index" n and suggested that the possibility of obtaining n from the viscosities of an oil at any two temperatures should be investigated. To achieve this end, the general equation

$$n = \frac{\log v_1 - k}{\log v_2}$$

had to be analysed to see how n and k calculated from two viscosity values at temperature intervals T_1 and T_2 different from 100° and 210° F differed from each other and from those calculated at 100° and 210° F. It was found that k, contrary to expectations of Part I, varied with the temperatures T_1 and T_2 and was indeed a complex function of (T_1), (T_2), and $\left(\frac{T_2}{T_1}\right)$.

Further calculations have shown that k also varied with the type of the

oil considered for the same values of T_1 and T_2. Efforts to effect a correlation between k and the temperature interval for oils of various viscosity indices have led to the conclusion that such attempts would complicate the calculation of n and render the method almost unworkable. The extrapolation of viscosities to those at 100° and 210° F, on the other hand, may be possible by means of Walther's equation or the A.S.T.M. chart, so long as viscosities of an oil at two temperatures are known. The procedure is based on the assumption that Walther's equation or its modification

$$\log \log (v + 0{\cdot}6) = m \log T + b$$

on which the A.S.T.M. chart is based does hold for the temperature interval under consideration. Computation by means of Walther's equation is rather time consuming and certainly not so convenient as when the A.S.T.M.

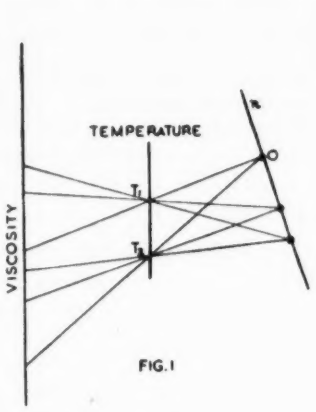


FIG. 1

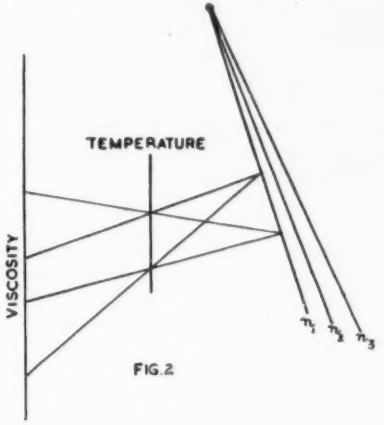


FIG. 2

chart is used. The procedure would then be to obtain the viscosities at 100° and 210° F from the chart and to calculate n from the expression given in Part I, namely

$$n = \frac{\log v_{100} - 0{\cdot}4336}{\log v_{210}}$$

The foregoing methods, although capable of yielding correct values of n, are not in themselves direct nor rapid enough for general laboratory work. It has been found that perhaps the most direct method for the determination of n from viscosities at any two temperatures is the following nomographic method.

THE NOMOGRAM. Examination of Walther's equation has revealed that when kinematic viscosities, v, and absolute temperatures, T, are plotted as log log $(v + 0{\cdot}6)$ and log T respectively on two parallel scales as shown in Fig. 1 the lines connecting viscosities to their corresponding temperatures for each oil will intersect at a point which is characteristic of the oil, and its position with respect to the viscosity and temperature axes is some function of the constants m and b of Walther's equation. The existence of such a

polarity may still be true if the parallel scales are made oblique by suitable transformation.[3] In this nomogram, however, parallel scales of kinematic viscosity in centistokes and absolute temperature plotted as log log ($v + 0{\cdot}6$ and log T have been used. From the preceding it would follow that given its viscosities at any two temperatures the viscosities of an oil at other temperatures may be ascertained by connecting point O, which is located by the intersection of the two given viscosity–temperature lines, to any temperature on the log T scale and reading the required viscosity where this line cuts the centistoke scale.

A further step in the construction of the nomogram has been to obtain the locus of such characteristic points as O, for oils having the same values of n. It was found that the loci for various values of n are straight lines intersecting at a point and exhibiting polarity as shown in Fig. 2.

The foregoing steps have led to the construction of the nomogram which is given in the accompanying chart. The determination of the rational viscosity index n for an oil is carried out by connecting any two viscosities of the oil to their respective temperatures. The position of the point of intersection in the family of n loci determines the value of n. The point of intersection may also be utilized for determination of viscosities of the oil at other temperatures as described in previous paragraphs. The values of n may be converted into Dean and Davis V.I. by the empirical formula which appeared in Part I, namely

$$\text{V.I.} = (60 - \text{antilog } n)\, 3{\cdot}63$$

or directly by the curve representing V.I. as a function of n which is included in the nomogram for this purpose.

Department of Chemical Engineering,
The University,
Birmingham.

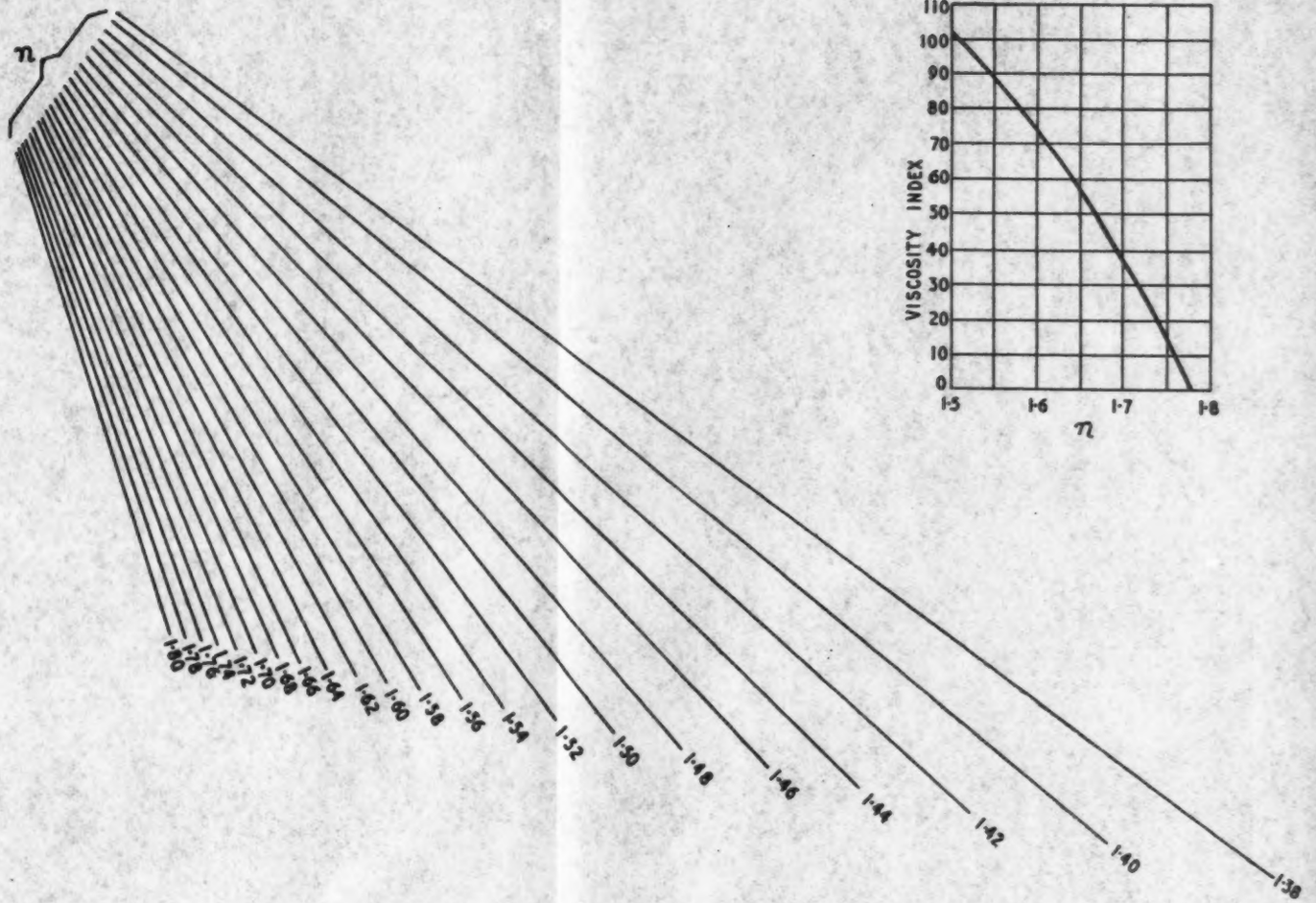
October 1947.

References.

[1] Hardiman, E. W., and Nissan, A. H. *J. Inst. Petrol.*, 1945 **31**, 255–270.
[2] Lapitzky, M. M. Private communication.
[3] Groff, J. "Proceedings of the general discussion on lubrication and lubricants," 1937. The Institution of Mechanical Engineers, *Vol. II*, 317.

KINEMATIC VISCOSITY - CENTISTOKES
20000000
10000000
5000000
2000000
1000000
500000
200000
100000
50000
20000
10000
5000
3000
2000
1000
500
300
200
150
100
75
50
40
30
20
15
10
8
6
5
4
3
2

TEMPERATURE
°F °C
0
50
100
150
200
210
230
-10
0
30
100
120


n
1·80
1·78
1·76
1·74
1·72
1·70
1·68
1·66
1·64
1·62
1·60
1·58
1·56
1·54
1·52
1·50
1·48
1·46
1·44
1·42
1·40
1·38

VISCOSITY INDEX
110
100
90
80
70
60
50
40
30
20
10
0
1·5
1·6
1·7
1·8
n

[To face p. 30.

DEVELOPMENTS IN PAINT OIL EXTENDERS.

By D. H. Tullis (*Member*).

Introduction.

The shortage of vegetable drying oils, particularly linseed oil, during the years 1942–45, led to a nation-wide search for substitutes and extenders. In this search the petroleum industry directed its efforts to the utilization of aromatic petroleum residues. Under the auspices of the Extracts Section of the Petroleum Board, some degree of success was obtained in the application of certain Edeleanu extracts as linseed-oil extenders in the manufacture of paints, core oils, and putty. A decided disadvantage of these extracts was the comparatively long drying time, which could only be offset by the use of increased amounts of drying accelerators such as metallic naphthenates, which in turn gave rise to other disadvantages for the paint manufacturer, since

(*a*) as the amount of naphthenate driers should be kept to a minimum, addition of excessive amounts results in paint films which rapidly developed brittleness and other defects; and
(*b*) increasing amounts of metallic naphthenates cause a marked degree of darkening and so limit the application of the extender to dark-coloured paints.

Although these aromatic petroleum residues were actually used to eke out the meagre supplies of linseed oil, their use was unsatisfactory in many respects, particularly with regard to weather resistance and colour. Thus, they were mainly used in low-grade paints and distempers which, it is reported, were all subject to marked " crocodiling " and " chalking."

The linseed-oil supply position has improved but little since the end of the war, and the price level is so high that the necessity for linseed-oil extenders continues. Whilst the aromatic petroleum residues may be considered as a necessary evil, the possibility must not be overlooked of the petroleum industry producing an extender or substitute which may even compete with linseed oil on its own merits.

Some of the more marked deficiencies of aromatic petroleum residues when intended for use in paints and distempers, are :

(1) their comparatively long drying times necessitates the use of increased amounts of metallic driers, with the attendant disadvantages;
(2) their dark colour limits the application to dark-coloured products;
(3) they undergo no real drying process in the manner in which the oils normally used in paint formulations become dry in the presence of air or oxygen, their drying process being more exactly described as " setting ";
(4) their use gives rise to rapid " crocodiling," " chalking," and darkening of the paint film;
(5) they have little capacity for the acquisition of " body " on heat-treatment under normal varnish-making conditions.

The purpose of this paper is to report upon some of the observations made during experiments which were carried out with a view to overcoming some of the more marked deficiencies of aromatic petroleum extracts, when these are utilized in the manufacture of paints.

The dark colour may, in general, be considerably improved by conventional acid treatment followed by clay treatment. The improvement, however, is limited by the fact that acid treatment tends to remove those unsaturated hydrocarbons which in themselves are largely responsible for whatever drying properties the extract might have. This lighter colour of the extract is itself of little benefit to the paint manufacturer, since relatively large amounts of metallic driers must still be used to compensate for the longer drying time of the extract, and the colour of the paint is affected more by the drier than by the extract, whether or not the colour of the latter has been improved by additional refining.

It should be pointed out that the extracts referred to here were in all cases further refined by acid and clay treatment, as one of the primary objects of these investigations was to develop an extender which could be used in very light-coloured and even white products, with only the amount of metallic drier which would be used in a normal linseed-oil-paint formula.

In attaining that objective, another petroleum product, normally amounting to a waste product, was found to impart to the extract extender properties which the extract extender did not in itself possess except in a very limited degree. This other product was recovered from the bottoms produced by re-running stabilized clay-treated sour cracked gasoline from a thermal cracking plant and will henceforth be referred to as "polymer."

Extracts.

The extracts concerned were all obtained from the Edeleanu solvent-refining process, the plant-charging stocks ranging from light spindle to heavy engine distillates. No one particular refined extract was used, blends of varying proportions being made to a viscosity of 140 sec Redwood I at 140° F. In general, these extracts were produced from a Peruvian low-cold-test crude—a naphthenic-base crude—which is particularly suitable for the preparation of a linseed-oil extender, since oils which are naphthenic in character have good pigment-wetting properties.[1] Extracts from other crudes, viz., Peruvian high cold test (a paraffin-intermediate crude) and Eakring (an intermediate-paraffin crude) were also used, but as will later be shown, these had strict limitations. All such Edeleanu extracts were further refined with sulphuric acid in concentrations varying from 85 to 95 per cent, followed by contacting with activated fuller's earth. Characteristics typical of such an aromatic extract are:

Sp. gr. at 60° F	0·980
Flash point, P.M. (closed), ° F	325
Viscosity, Redwood I at 140° F, sec	142
Colour, A.S.T.M.	4½
Pour point, ° F	5
Acidity: total, mg. KOH/gm	0·03
inorganic, mg KOH/gm	Nil
Iodine value, I.P. 84/45 (T)	59
Drying time, I.P. 93/44 (T), hr	54

"Polymer."

This material is a much less familiar product than is an Edeleanu extract. The cracking or thermal decomposition of petroleum under normal conditions yields unsaturated hydrocarbons—mono-olefins and diolefins—

which can be polymerized to resinous materials. Treatment of sour cracked gasoline with refining agents such as sulphuric acid, activated earths, or zinc chloride also effects the conversion of unsaturated hydrocarbons of this type into resins, and as these latter products are by-products of a large industry and could be available in appreciable quantities (they amount to about 0·5 per cent of the charge to a thermal-cracking plant) the separation of high-grade products offers commercial possibilities. But so far, little success appears to have attended efforts to utilize these by-products of cracking and refining, the normal practice being to recycle the re-run gasoline bottoms through the cracking coils or the flash chamber and so eventually lose them to gas, coke, and/or fuel, the amount of gasoline produced by their cracking being very small.

Also, in thermal-cracking processes, pressure exerts a considerable influence on the character of the products formed, and causes the polymerization and condensation of olefins initially formed. As such reactions are bimolecular they are favoured by increase in pressure.

By a combination of these two types of polymerization, viz., pressure and treatment, the unsaturated hydrocarbons are largely eliminated from the cracked gasoline in the form of high-boiling unsaturated residues in the re-run bottoms. These high-boiling residues are, in fact, analogous to the gums formed in cracked gasoline on storage and, of course, their removal greatly increases the storage stability of cracked gasoline. It has been known for some years that these gums have some resemblance to linseed oil in their physical characteristics, although their chemical composition is entirely different. Thus, by stripping the re-run bottoms of the heavier gasoline ends, these high-boiling residues are recovered as a brown mobile liquid. This is the crude "polymer," and a representative analysis is :—

Sp. gr. at 60° F	0·940
Flash point, P.M. (closed), ° F	162
Viscosity : Redwood I at 70° F, sec	248
Redwood I at 140° F, sec	53
kinematic at 77° F, cs	48·44
Colour, A.S.T.M. (0·1% in CCl_4)	2—
Pour point, ° F	Fluid at 0
Acidity, mg KOH/g	0·02
Aniline point, I.P. 2/47, ° C	39·5
Iodine value, I.P. 84/45 (T)	300
Drying time, I.P. 93/44 (T), hr	2
Distillation, I.P. :	
I.B.P.	166° C
at 200° C, per cent	4
at 225° C, per cent	15
at 250° C, per cent	26
at 275° C, per cent	41
at 300° C, per cent	66

A somewhat similar material was obtained by Potolovski and Atal'yin in their studies of the polymerization of a mixture of the lower gaseous olefins by aluminium chloride. Their product, obtained after 10 days at room temperature, contained 40 to 45 per cent of gasoline and kerosine hydrocarbons and 50 to 55 per cent of heavier oil and the residue obtained on vacuum distillation was a drying oil formed by the polymerization of di-olefins with olefins.[2]

Improvement of Aromatic Extract Extenders.

It was found possible to improve the drying time of an aromatic petroleum extract without recourse to the addition of metallic naphthenates, by the incorporation of "polymer." The improvement was quite marked, and the effect of "polymer" was much superior, from the view-points of drying-time and colour of the resultant product, to that obtained by the use of cobalt naphthenate. That the improvement was generally applicable is shown in Tables I–III, which depict results obtained with three different extracts, these being :—

E.1—an extract from Peruvian low-cold-test stock;
E.2—an extract from an unknown stock, which did not respond to acceleration of drying by cobalt naphthenate;
E.3—various blends of E.1 with Pool Grade 5b extract from Eakring stock.

The viscosity of each of these extracts was 140 sec Redwood I at 140° F.

Table I.

Extract E.1.

	Neat.	+ 1% "Polymer."	+ 3% "Polymer."	+ 5% "Polymer."	+ 10% "Polymer."	+ 1% Co Naph.
Colour, A.S.T.M. .	4½ −	7	8 +	8 +	8 +	8 +
Drying time, hr .	54	36	32	24	20	40

The increase in drying time with increasing amounts of cobalt naphthenate, as shown in Table II, is in agreement with published results of the effect of cobalt naphthenate on the drying time of linseed oil.[3] In regard to Table III it was observed that with blends containing more than

Table II.

Extract E.2.

	Neat.	+ 0·3% "Polymer."	+ 0·5% "Polymer."	+ 0·7% "Polymer."	+ 1% "Polymer."	+ 5% "Polymer."	+ 0·3% Co. Naph.	+ 0·5% Co. Naph.	+ 1% Co. Naph.	+ 2% Co. Naph.	+ 3% Co. Naph.	+ 1% Pb. Naph.	+ 1% Mn. Naph.
Colour, A.S.T.M. .	6−	6	7−	7	8−	8+	7−	8−	8+	8+	8+	8−	8−
Drying time, hr .	60	60	60	55	55	40	60	60	60	70	70	60	60

Table III.

Extracts E.3 (Blends of Eakring Extract in E.1).

% Eakring Extract :	5.	5.	10.	10.	15.	15.	20.	20.	30.	30.
% "Polymer" :	Nil.	1.	Nil.	1.	Nil.	1.	Nil.	1.	Nil.	1
Colour, A.S.T.M. .	3	6	3	6	3½−	5	3½−	5	4	6−
Drying time, hr .	53	49	67	62	68	60	73	68	94	82
Pour point, ° F .	15	15	20	20	20	20	25	25	40	40

15 per cent Eakring extract the surface of the dried film exhibited a "rippled" appearance. This was purely a surface phenomenon, most

probably due to the crystallization of wax, and in no way was the film broken or distorted. This same effect was obtained when another waxy extract from Peruvian high-cold-test stock was used in an extender, and so it would appear that extracts from waxy stocks have only a limited application in extenders of petroleum origin, unless the wax content can be controlled to lower limits in the wax-rejection stage of the Edeleanu plant.

Although marked improvement in drying time of the extract extender is effected with only a small addition of " polymer," the resultant product is considerably darker in colour. Colour improvement of the " polymer " as recovered from the re-run bottoms by conventional contacting with an activated earth or charcoal is ineffective. Atmospheric distillation revealed that the most effective portion of " polymer," from the point of view of drying acceleration, is contained in the residue. This observation was also borne out by vacuum distillation at 25 mm Hg, but lighter-coloured material of similar drying properties was obtained. The degree of colour improvement obtained by this means was, however, quite insufficient. Satisfactory colour improvement was found to be possible by a process of percolation in dilution through a packed column of activated fuller's earth, the most efficient diluent in this process proving to be sludge spirit, but the most practicable one was straight-run gasoline. In this process of percolation, the " polymer " and diluent were mixed and fed to the top of the packed column; the filtered material issuing from the bottom of the column was collected in equal portions during the percolation, and all portions subsequently stripped of diluent by distillation. The comparative results which represent the percolation of 200 g of " polymer " through 300 g of activated fuller's earth, using 1000 ml of diluent, are shown in Table IV. Four cuts or portions were taken in each case, and on each colour and drying time determinations were made.

TABLE IV.

Diluent.	Cut.	Yield, %.	Total yield, %.	Colour, A.S.T.M.		Drying time of stripped " polymer," hr.
				Cut.	Stripped " polymer."	
Sludge Spirit	1	10·0	57·5	1½	3½	4
	2	18·5		2½	5 −	2
	3	20·0		3½	6	2
	4	9·0		4	8 +	2
Straight-run gasoline	1	11·0	55·5	2 −	4	4
	2	15·5		3	6	2
	3	15·5		4	7	2
	4	13·5		5 −	8 +	2

Although less than 60 per cent recovery of " polymer " is shown in Table IV, up to 95 per cent recovery can be obtained by further washing of the packed column, or by the initial use of a greater quantity of diluent. As the normal colour of the extract extender is about 5 A.S.T.M., it was decided that an equal colour would be satisfactory for the refined " polymer," and in a percolation to obtain maximum recovery of " polymer," 60 per cent yield of colour 5 A.S.T.M. material was obtained, and 35 per cent

of almost black material. The drying times of each of these fractions were, however, identical with that of the crude " polymer." As a result of numerous percolations it was found that only the first runnings had longer drying times than the crude " polymer "; the proportion of refined " polymer " with this longer drying time was about 10 per cent, and by blending with subsequent fractions up to at least 30 per cent, this was eliminated, the drying times of the blends all being the same as that of the crude " polymer." Although at first sight the clay consumption in this method of colour improvement would appear to be prohibitively high, such is not actually the case, since the spent clay from the percolation column can be reactivated satisfactorily for use in the clay contacting of the acid-refined Edeleanu extracts.

It was known that normal extract extenders darkened very considerably on weathering or on exposure to ultra-violet light, and comparisons between an extract from Peruvian low-cold-test stock and various blends of that extract with crude " polymer " were made, by exposure to a source of ultra-violet radiation for periods up to 15 hr. The colour change during exposure was followed by means of the Spekker absorptiometer, and Fig. 1 illustrates the rate of increase in optical density. The change was followed by measuring the absorption of light of several different wavelengths, and the curves shown in Fig. 1 * are those of results determined with a wavelength 5200 Å; other curves of the results produced from different wavelengths were of similar form.

It was observed that, in all cases, the blends containing " polymer " at first became lighter in colour, and in Fig. 1 it may be noted that there is an initial induction period, which, however, in the case of the extract alone (1471), is of very short duration. When using blends incorporating refined " polymer," the rate of increase of optical density was the same as with the crude " polymer," although the optical densities were of a lower order. From these curves it may be seen that the extract extender is very susceptible to the influence of ultra-violet light, and that the presence of small amounts of " polymer " appears to delay the start of deterioration, an advantage which was also apparent when the ageing of paints was being examined.

It had been considered probable that the type of checking known as " crocodiling," which occurs in paints containing extenders of petroleum origin, is due to the oxidation of the paint continuing after the drying stage. Experiments were conducted to examine the absorption of oxygen by linseed oil when adulterated with an extract extender, and with extract extenders incorporating small amounts of " polymer " or cobalt naphthenate, and to determine the effect of various inhibitors which might retard the oxidation. After preliminary work with an apparatus based on that used by Moureu and Dufraisse for similar experiments,[4] modifications were effected so that measurements could be made of the actual volume of oxygen absorbed instead of measuring the pressure drop. The apparatus consisted essentially of a 100-ml conical flask which was immersed in a thermostatically controlled water-bath, and to which was connected a gas burette and a dibutyl phthalate manometer to measure the volume decrease

* The extract from Peruvian low-cold-test stock is referred to in the legend of Fig. 1 as Extract 140.

at constant pressure. The oxygen-absorption curves obtained are shown in Fig. 2 and again the extract used in the experiments was one from Peruvian low-cold-test stock (Extract 140).

The shape and slope of the curves are influenced by the rate of oxygen diffusion through a thin layer of oil and the mixing of oxidation products; true reaction–velocity curves could have been obtained by vigorous agitation of the liquid. However, the type of oxidation under examination was that of a stationary film, and the desirable inhibitor one which would

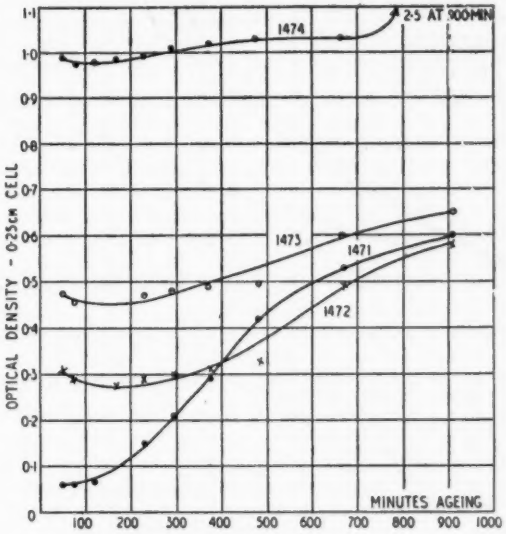


FIG. 1.

CHANGE OF OPTICAL DENSITY (5200 Å).

1471. Extract 140.
1472. „ „ + 1% polymer.
1473. „ „ + 2% „
1474. „ „ + 5% „

be active at the surface, and so the method adopted was eminently satisfactory.

These curves of oxygen absorption show that phenyl-α-naphthylamine was most effective in lowering the rate of oxidation. The increase in the amount of oxygen absorbed when " polymer " was included was slight and could be accounted for by the amount of oxygen absorbed by the " polymer " itself. The relative effects of " polymer " and cobalt naphthenate, when considered in conjunction with the drying times reported in Tables II and III, indicate that cobalt naphthenate is essentially catalytic in its action, being itself non-drying, whilst " polymer " owes its effectiveness in reducing the drying time of aromatic extracts to its own property of drying. In one of the preliminary runs using an aromatic extract with

1 per cent " polymer " but without linseed oil, it was observed that, after the absorption of 7 ml of oxygen by 15 g of the solution, the colour of the

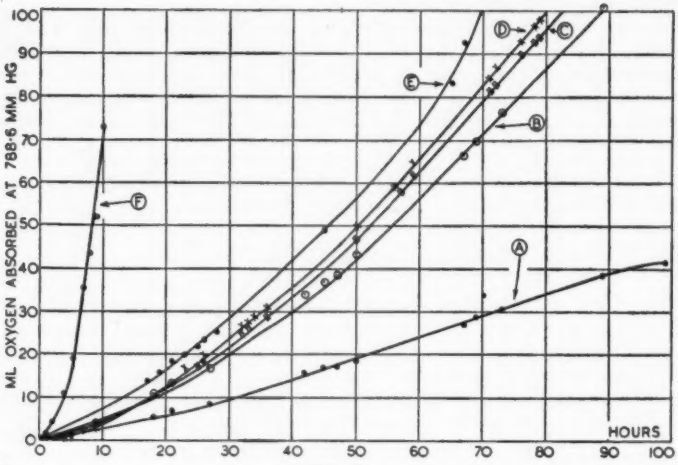


FIG. 2.

RATE OF OXYGEN ABSORPTION OF LINSEED OIL AND EXTRACT-CONTAINING ADDITIVES.

A. 75% linseed oil; 25% extract 140; 1% polymer (containing 0·005 mol phenyl-α-naphthylamine per 100 g mineral oil).
B. 75% linseed oil; 25% extract 140; 1% polymer (containing 0·005 mol phenyl-β-naphthamine per 100 g mineral oil).
C. 75% linseed oil; 25% extract 140.
D. 75% linseed oil; 25% extract 140; 1% polymer.
E. 75% linseed oil; 25% extract 140; 1% polymer (containing 0·005 mol diphenylamine per 100 g mineral oil).
F. 75% linseed oil; 25% extract 140; 1% cobalt naphthenate.

blend was much lighter, and on the basis of optical density had been reduced to that of 0·5 per cent solution of " polymer " in the aromatic extract. This is further evidence of the bleaching of " polymer " which occurs on oxidation, as previously mentioned.

APPLICATION OF AN IMPROVED EXTENDER TO PAINTS.

In the application of extenders of petroleum origin to paint, hand-mixing only of the ingredients was initially done, and although the paints so produced were reasonably suitable for exposure tests, they were unsatisfactory in other respects (mainly appearance in comparison with commercial products), but in later experiments the use of a laboratory ball-mill produced paints which were equal in appearance to commercial products of the same type. Although " polymer " satisfactorily improves the drying time of an extract and of a paint incorporating an extract extender, it cannot eliminate the necessity of using a metallic drier in a paint formula, although satisfactory paints can be obtained with the use of only the same amount of metallic drier as is required for equivalent linseed-oil paints.

The preparation of the paints was carried out in the following manner : finely ground cobalt naphthenate having been dissolved in white spirit, and the linseed oil and/or extender added slowly with thorough mixing, the pigment was added to the vehicle and the mix transferred to the laboratory ball-mill in just sufficient quantity to cover the porcelain balls. The grinding process was accomplished by rotating the mill for 6 hr at such a speed as to allow the balls to reach the highest point of the mill before falling. The various paints prepared were subjected to accelerated ageing tests, since this investigation was a " short-term " one, and although some natural weathering tests were carried out, these were of comparatively short duration and could only give results which were indicative and not necessarily conclusive; the test panels used were glass or aluminium plates 4 in by 8 in, and the paints were applied to the test panels by brush.

The accelerated ageing test employed was a slight modification of an ultra-violet-light test employed by a paint manufacturer. The lamp used was a Hanovia S. 500 arc-tube, and the test panels were arranged round the lamp symmetrically equidistant and 6 in from the lamp, one half of each panel being shielded from the rays of the lamp by a strip of opaque material impervious to ultra-violet light. The exposed paint was compared visually with the unexposed portion at prescribed intervals; in addition the test panels were immersed in water after varying periods of exposure, examined, and submitted to further radiation. It was not possible to follow the degree of ageing with the Spekker absorptiometer nor to apply a method of absolute colour measurement, because of the opacity of the paints and since if sufficient light had been transmitted, then it would have been dispersed by the pigment. Therefore visual examination of colour changes had to be made, with the attendant difficulties of interpretation.

The linseed-oil-paint formula which was mainly used as the basis for comparison was a commercial one generally known as " genuine zinc-white paint " and had the composition :—

Zinc oxide	60% by weight
Linseed oil	34% " "
White spirit	5% " "
Cobalt naphthenate	1% " "

although other comparisons were made with " white-lead paint " as the base. The vehicle, linseed oil, was replaced in whole or in part by varying blends of " polymer," refined as herein described to a colour of 5 A.S.T.M., and an aromatic extract from a naphthenic-base distillate, of composition similar to that already quoted.

All paints were applied to the test panels by brush, and a quick and easy comparison of consistency and flow characteristics or " brushability " was thus possible. When paints were prepared with complete substitution of the linseed-oil vehicle by refined " polymer " the mobility of the paint was very adversely affected and to obtain the same brushing consistency as for the parallel linseed-oil paint, 1·5 times as much refined " polymer " as linseed oil had to be used. This was quite contrary to expectations, as the viscosities of linseed oil and refined " polymer " were 110 and 40 cs respectively at 77° F. It was established that " polymer " did not polymerize to any great extent during the grinding process, the viscosity

of the paint medium being determined before and after 6 hr agitation in the ball-mill, and the rise in viscosity only amounted to 3 to 4 per cent. Surface-tension measurements showed little difference between linseed oil and "polymer," but the addition of small quantities of surface-active agents revealed the consistency anomalies to be due to differences in wetting power. In this respect 0·3 per cent of oleic acid satisfactorily reduced the brushing consistency of the "polymer" paint to that of the linseed-oil paint. When no more than about 50 per cent substitution of linseed oil by "polymer" is attempted this consistency anomaly does not arise and surface-active agents are unnecessary.

To tabulate observations made on the individual ageing of the many paints prepared would serve little purpose here. The following are the conclusions drawn from the ageing tests.

Crocodiling.

This was not found to occur in paints containing an extract extender derived from a naphthenic-base crude oil and/or "polymer." Consequently, the use of oxidation inhibitors was not very deeply investigated, although it was observed that the use of phenyl-α-naphthylamine or phenyl-β-naphthylamine increased the degree of yellowing of the paint film on ageing. The proportion of inhibitor was quite small, amounting to only 0·005 mol/100 g of extender, which was present in the vehicle to the extent of 25 per cent by weight.

Blistering and Chalking.

In paints containing an extract extender small round blisters were found to occur after only a few hours ageing, but the presence of only 1 per cent "polymer" in the extender produced a paint which was still free from blisters after 48 hr ageing. Chalking did not occur after 48 hr ageing in paints containing an extract-1 per cent "polymer" extender, but was severe with the corresponding linseed-oil paint after only 24 hr similar ageing.

Gloss and Colour.

All hard-dry paints with up to 25 per cent substitution of the linseed oil with extract-"polymer" extenders possessed higher gloss than the genuine linseed-oil paint, and the paints containing the extract-"polymer" extenders were more resistant to the effects of ageing by ultra-violet light and water, their gloss outlasting that of the linseed-oil paint. Colour deterioration on ageing was more marked with paints incorporating an extract extender, but the presence of refined "polymer" in the extender improved the initial colour and degree of colour deterioration progressively with increasing amounts of "polymer." 50 per cent "polymer" in the extender produced a paint which compared very favourably with the linseed-oil paint, particularly with regard to colour deterioration.

Hardness of the Paint Film.

The hard-dry films of paints containing an extract extender were slightly less resistant to scratching than the linseed-oil paints, and increasing

amounts of " polymer " in the extract extender did not have any appreciable effect until the amount of " polymer " reached 25 per cent, beyond which the films became markedly softer. For this reason it would not be commercially practicable to employ more than 25 per cent of " polymer " in the extender, nor to attempt appreciable replacement of linseed oil by the " polymer " alone, unless it is found possible to incorporate some film-hardening agent.

From these investigations and observations it would appear that " polymer " has possible commercial applications in the manufacture of paints, either by itself or in admixture with normal extract extenders. In applications other than in paint-oils, " polymer " appears to possess properties which might permit its utilization in other products, such as lithographic inks, which normally employ linseed or other drying oils.

ACKNOWLEDGEMENT.

The author's thanks are due to Lobitos Oilfields Ltd. for permission to publish these observations on work carried out in their research and sales laboratories.

References.

[1] Healey and Ivanovsky. *J. Inst. Petrol.*, 1947, **33**, 285.
[2] Carleton Ellis. " Chemistry of petroleum derivatives," Vol. II, p. 203.
[3] Curwen, –. *Paint Manufacture*, Feb. 1936.
[4] Bailey, –. " Retardation of chemical reactions," 9, 1, 112.

THE HYDROCARBON TYPE COMPOSITION OF CRACKED GASOLINES.

By H. C. Rampton (Associate Member).

Summary.

A method of hydrocarbon-type analysis has been developed for cracked gasolines and similar products which permits the determination of groups of hydrocarbons :—

(*a*) Aromatics
(*b*) Naphthenes.
(*c*) Paraffins.
(*d*) Alkenes (non-cyclic olefins).
(*e*) Cyclenes (cyclic olefins).

The quantity of individual members of each of these hydrocarbon groups can be assessed in most cases since the analyses are carried out on highly fractionated cuts of selected boiling range.

The procedure of the method has as its basis the following scheme :—

(*a*) Separation of naphthenes and paraffins from olefins and aromatics by selective adsorption followed by naphthene and paraffin determination on fractions of selected boiling range;
(*b*) Hydrogenation of original cracked gasoline to convert olefins to paraffins and naphthenes without hydrogenation of the aromatic hydrocarbons.
(*c*) Determination of the aromatic hydrocarbons on fractions of selected boiling range prepared from the hydrogenated cracked gasoline.
(*d*) Removal of aromatics in hydrogenated cracked gasoline by selective adsorption followed by paraffin and naphthene determination on fractions of selected boiling range.
(*e*) Estimation of alkenes and cyclenes from differences in the analyses of corresponding boiling range fractions in (*a*) and (*d*).

Introduction.

The development of methods of analysis, by which the hydrocarbon-type composition of petroleum products may be determined, has received considerable attention in recent years. The exacting needs of the high-efficiency I.C. aircraft engines used in the last war focused such attention on the chemical make-up of straight-run distillates within the boiling range of aviation fuels. The complete analysis in terms of individual hydrocarbons is extremely difficult in view of the large number of possible isomers. The normal course, therefore, is to determine the contents of groups of hydrocarbons of certain types, *e.g.*, paraffins, aromatics, and naphthenes. The naphthenes are the fully saturated cyclic carbon-ring compounds, and in the absence of evidence to the contrary are considered to contain five- and six-membered rings only.

Fractional distillation is the primary tool employed in hydrocarbon-type analysis, and much progress has been made in the design and fabrication of ultra-efficient columns. Using such columns, it is possible to separate a gasoline into cuts of narrow boiling range, analysing each subsequently for aromatic, paraffin, and naphthene contents. However, it has been realized that, due to abnormal vapour-pressure relationships between aromatics and certain paraffins and naphthenes, it is advantageous to remove the aromatics prior to distillation. Selective adsorption is a more satisfactory

procedure than exhaustive acid washing for removal of aromatics. By simple percolation through a silica-gel-packed column, an aromatic-free percolate is obtained, consisting of the unchanged naphthene–paraffin component, which can be fractionated and analysed.

With the increasing employment of petroleum as a source of raw materials for the manufacture of synthetic chemicals and the like, it is of considerable importance to know the hydrocarbon make-up of other than straight-run products, *e.g.*, those resulting from processes such as cracking or reforming, etc. The essential difference between straight-run and cracked or reformed gasolines is the presence in the latter of an additional class of hydrocarbons, namely, the unsaturateds, or olefins. The object of the investigation described in the present paper has been the development of a satisfactory method of hydrocarbon-type analysis of mixtures of aromatics, paraffins, naphthenes, alkenes, and cyclenes throughout the gasoline boiling range, on similar lines to that employed for straight-run materials.

The principle most commonly followed for the determination of olefins in hydrocarbon mixtures involves the measurement of the extent of reaction with halogens according to the equation :—

$$R{-}CH{=}CH{-}R + Br_2 = R{-}CHBr{-}CHBr{-}R \quad . \quad . \quad (1)$$

As numerous investigators have shown, in the presence of excess halogen, side reactions can also occur, especially those of substitution in the aromatic nucleus :—

$$C_6H_5{\cdot}R + Br_2 = C_6H_4Br{\cdot}R + HBr \quad . \quad . \quad . \quad . \quad (2)$$

As a result, analytical procedures fall into two main classes. The first class follows the method of McIlhiney,[1] who suggested the addition of excess halogen with subsequent correction for substitution by titration of any acid formed. The second class is headed by the well-known Francis method,[2] in which the addition of halogen is controlled to minimize the excess and so suppress the substitution reaction.

Suggested procedures based on other principles include solution in sulphuric acid of specified concentration,[3, 4] reactions with mercuric salts,[5, 6] ozone,[7] thioglycollic acid,[8] and sulphur monochloride.[9]

Methods of estimating aromatic hydrocarbons, in general, necessitate their removal by chemical means and comparison of physical properties of original and non-aromatic constituents,[10, 11, 12] although specific dispersion measurements (hydrogen F and C lines at 20° C) made on original samples have been considered,[13] with correction factors for olefinic content based on B.N. determinations.

Hydrocarbon-type Analysis.

The methods mentioned above are normally applied to determinations of bulk olefin and aromatic contents, but have been applied by other workers to the analysis of fractions of narrow boiling range prepared by distillation of the cracked gasoline. In this way, a distribution of hydrocarbon types throughout the boiling ranges can be obtained. By judicious selection of cut points, it is possible to arrive at a detailed composition in terms of individual groups. Due to the astronomically large number of possible isomers, particularly of the unsaturateds, and to the shortcomings

of the available methods of estimation of degree of unsaturation, the results are considered merely as approximations. The spread of boiling point of the olefins brings an additional complication. The paraffins are separable by boiling range alone into well-defined sections, *i.e.*, *iso*hexanes, *normal* hexane, *iso*heptanes, *normal* heptane, *iso*octanes, etc. The aromatics and naphthenes, too, fall into distinct subdivisions determined by molecular weight–boiling point relationships. In the case of the olefins, however, the magnitude of the spread of boiling point of isomers renders any subdivision well nigh impossible. This fact is illustrated in Table I.

TABLE I.

Boiling Points (°C.) of Isomers.

Number of carbon atoms per molecule :	6.	7.	8.	9.
Paraffins . . .	49·7–68·7	79·3– 98·4	99·2–125·6	122·2–150·7
Naphthenes . . .	72 –80·8	87·5–103	112 –130·8	132·7–157·2
Alkenes	41·2–82	76 –115	100 –140	114 –167
Cyclenes	67 –89	78 –121	99 –153	129 –161

The direct outcome of such overlaps is that a procedure based on a distillation of the original cracked gasoline cannot yield accurate information regarding the shape and size of the olefin molecules present, information of the utmost value in almost all applications of cracked gasoline.

A scheme of analysis has been developed, therefore, which overcomes these difficulties. The first step is the isolation of the naphthenes and paraffins and is accomplished by the adsorption of the aromatics and olefins on silica gel. Determination of the distribution of naphthenes and paraffins is readily accomplished by fractionation and analysis employing the methods used for straight-run distillates.

The determination of the aromatic hydrocarbons is accomplished by hydrogenation of the sample under conditions proved to effect complete saturation of the olefins without converting the aromatics to naphthenes. The nature and distribution of the aromatic hydrocarbons can then be ascertained by any method applicable to straight-run distillates, such as fractionation combined with ultra-violet adsorption spectra of suitable fractions.

The unsaturated hydrocarbons comprising alkenes and cyclenes are determined by examining a further portion of the hydrogenated product. On hydrogenation an alkene is converted to a paraffin and a cyclene to a naphthene, and under the conditions employed the carbon linkages are not disturbed. The hydrogenated product can be readily de-aromatized by silica-gel adsorption to leave only paraffins and naphthenes; these hydrocarbons consist of those originally present in the sample and those derived from the alkene and cyclenes on hydrogenation. By determination of the quantity and distribution of the naphthenes and paraffins in the hydrogenated product and from similar knowledge of these hydrocarbons in the original samples, the concentration and distribution of the naphthenes and paraffins derived from the cyclenes and alkenes can be calculated by difference.

Isolation of Naphthenes and Paraffins.

The isolation of the naphthenic and paraffinic constituents of cracked gasolines was accomplished by development of an extension of the technique of chromatographic or selective adsorption, already well known and employed for the analysis of straight-run naphthas in terms of hydrocarbon type.[14, 15] Samples of straight-run naphthas are percolated through columns containing solid adsorbents. The individual groups of hydrocarbons differ markedly in their behaviour towards such adsorbents. While the aromatic hydrocarbons are strongly adsorbed, the naphthenes and paraffins

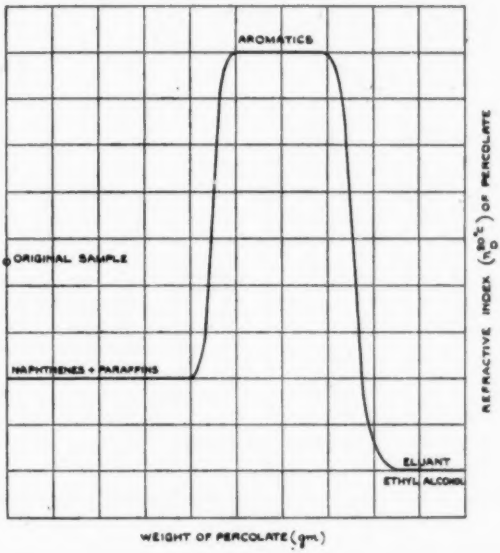


Fig. 1.

CHARACTERISTIC ADSORPTION CURVE—STRAIGHT-RUN NAPHTHA WITH ELUANT.

are but weakly adsorbed and do not appear to differ among themselves as a whole. As a result the first percolates obtained are composed of naphthenes and paraffins only, and the presence of aromatic compounds is not observed until the adsorbent is fully saturated with respect to the latter type of hydrocarbon. By charging to the adsorbent column the requisite amount of naphtha to saturate the adsorbent with respect to aromatics, it is possible to isolate the naphthene plus paraffin component in almost quantitative yield. This is achieved by eluting the column with a solvent or eluant which is more strongly adsorbed than the aromatic hydrocarbons. The characteristic plot of refractive-index values of successive percolates versus yield in such selective adsorption procedures, using ethyl alcohol as eluant, will be seen in Fig. 1. The adsorbent utilized is, in almost all cases, silica gel.

Attempting similar adsorptions with cracked gasolines, the characteristic curves obtained are somewhat similar (see Fig. 2), but it is readily apparent that complete separation of component groups of hydrocarbons is not achieved in such cases, the unsaturated hydrocarbons present being distributed between the naphthene–paraffin and aromatic constituents. It was thought that isolation of the naphthene–paraffin component might be

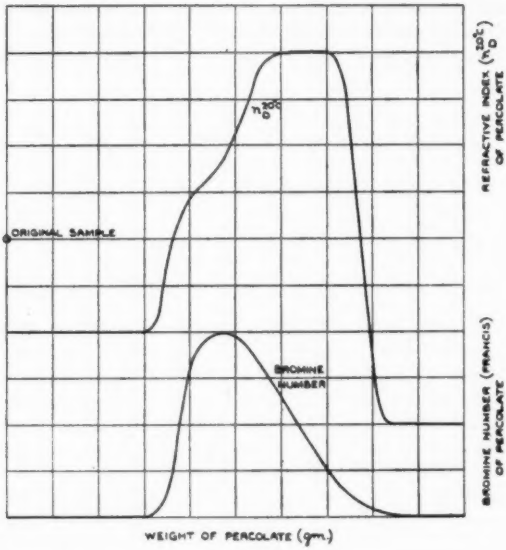


FIG. 2.

CHARACTERISTIC ADSORPTION CURVES—CRACKED GASOLINE WITH ETHYL-ALCOHOL ELUANT.

made possible by replacement of these hydrocarbons by some intermediate eluant. Such an eluant would be satisfactory if the following requirements were met :—

(*a*) aromatic and unsaturated hydrocarbons to be absent;
(*b*) the boiling range to be outside that of the cracked gasoline.

A kerosine cut was prepared, therefore, the initial boiling point of which was 180° C when distilled on a 40-plate fractionating column * and the aromatic hydrocarbons removed by exhaustive washing with concentrated sulphuric acid. A final check was made to confirm the absence of aromatics by selective adsorption. A cracked gasoline sample was distilled to 175° C overhead temperature (40-plate fractionating column—reflux ratio 40/1) and the 45 to 175° C cut segregated. It was thereby ensured that the

* The 40-plate fractionating column referred to throughout this paper consists of a 5-ft section of 1-in diam tube, packed with ¼-in single-turn glass helices, equipped with variable take-off device and electrically controlled lagging for maintenance of adiabatic conditions.

kerosine eluant was of higher boiling point than the cracked gasoline cut for the test.

The adsorption column consisted of two 6-ft sections (2-in I.D.) of pyrex-glass tubing, coupled in series (see Fig. 3). The charge of silica-gel used amounted to 4000 g of mesh size 30 to 70 and was activated prior to use by heating at 400° C for 3 hr. A quantity of 500 g of the cracked gasoline 45 to 175° C cut was introduced into the column, followed by kerosine eluant as prepared above, until the refractive indexes of successive

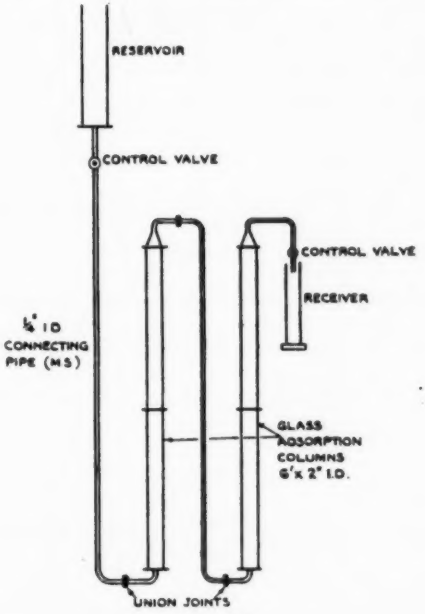


FIG. 3.

ADSORPTION COLUMN FOR CRACKED GASOLINES.

percolates attained a steady value, identical with that of the neat kerosine eluant. The rate of percolation was maintained at 120 to 150 ml/hr throughout. Previous workers in selective adsorption have, in general, used gravity flow, *i.e.*, downward flow through the adsorption column. In the present work, upward-flow conditions were preferred on the score of more complete wetting of the adsorbent and less likelihood of trapping air and creating "pockets" or "channelling." By distillation to 175° C overhead in 40-plate fractionating columns the unadsorbed constituents of the cracked gasoline cut were recovered from the successive percolates. Percolation was continued until no yield of distillate to 175° C was obtained, indicating that all the naphthene and paraffin hydrocarbons present in the cracked gasoline cut had been eliminated from the adsorption column. The distillates were found to be completely saturated (Francis B.N. = nil)

and proved to be aromatic-free when analysed by a variety of methods. The individual and cumulative yields of distillates are shown in Fig. 4, whence it is evident that exhaustive extraction of the silica gel with the kerosine eluant has been attained, and that the bulked yield of distillates did, in fact, consist of the naphthene and paraffin hydrocarbons originally

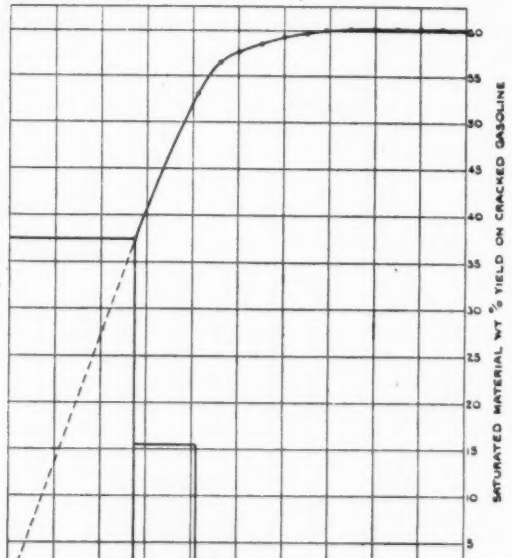


FIG. 4.

ADSORPTION OF CRACKED GASOLINE WITH KEROSINE ELUANT—YIELDS OF SATURATED MATERIAL.

present in the cracked gasoline sample. The percentage naphthene plus paraffin content by weight could then be calculated.

$$\text{Weight per cent naphthene plus paraffin content} = \frac{\text{Total weight of distillate to 175° C}}{\text{Weight of sample charged}}.$$

The amount of silica gel adsorbent required may be based on an adsorptive capacity of 5 g aromatic plus unsaturated hydrocarbons per 100 g silica gel, and the production of a minimum quantity of 300 g of naphthene plus paraffin component was attempted.

The yield of distillate was distilled through a fractionating column *

* The 25-plate column referred to throughout this paper is essentially the cupped stainless steel gauze spiral packed unit described by Lecky and Ewell.[17]

(not less than 25 theoretical plates) at a reflux ratio greater than 40 : 1, the dynamic hold-up of the column being not greater than 5 per cent of the charge. T.B.P. data on a weight basis were recorded and specific cuts segregated, of boiling ranges :—

(i) I.B.P. (45° C)–66° C.
(ii) 66– 70° C.
(iii) 70– 75° C.
(iv) 75– 85° C.
(v) 85– 95° C.
(vi) 95–109° C.
(vii) 109–120° C.
(viii) 120–130° C.
(ix) 130–150° C.
(x) Residue (150–175° C).

The density at 20° C in g/ml (accuracy $\pm$ 0·0001 g/ml) and the refractive index at 20° C, sodium D line (accuracy $\pm$ 0·0001) of each cut were determined, and specific refractions calculated according to the formula :—

$$\frac{n^2-1}{n^2+2} \times \frac{1}{d}$$ where d = density at 20° C g/ml :
n = refractive index at 20° C (sodium D line).

By linear interpolation, using mean values for the specific refractions of the naphthenes and paraffins, assumed to be present from consideration of boiling range, the naphthene and paraffin contents of each cut were determined and expressed as weight percentages of the sample. Fig. 8 gives a plot of mean specific refraction values versus boiling point.

The recovery of the aromatics and olefins retained on the silica gel offered a possible means of completing the analysis. Desorption of the column, using an eluant more strongly adsorbed than either aromatics or unsaturateds, should have yielded, theoretically, the content of these two classes of hydrocarbons present in the original cracked gasoline. Ethyl and methyl alcohols were tried as desorbing eluants, but manipulative losses and difficulties encountered during the work-up of the alcohol–hydrocarbons mixture proved too great. It must be stressed, also, that the boiling-point disadvantages mentioned earlier would still apply in the case of a distillation of the paraffin- and naphthene-free gasoline, even if it were possible to isolate such material. No further work on these lines was attempted.

Hydrogenation of Alkenes and Cyclenes.

The estimation of the aromatic contents of a straight-run gasoline presents no difficulty. The complete hydrogenation of the alkenes and cyclenes of cracked gasoline produces a saturated material which is virtually a straight-run product. The primary aim of the particular hydrogenation procedure employed in this investigation was the conversion of the alkenes and cyclenes to the corresponding paraffins and naphthenes without change of the paraffins and naphthenes already existing in the cracked gasoline. A secondary but equally important aim was that the aromatics of the hydrogenated product would be identical with those present in the original

sample. The bearing of these considerations on the method of analysis will be explained in detail later.

A few preliminary experiments with known hydrogenation catalysts under varying conditions were carried out. As a result, the small hydro-

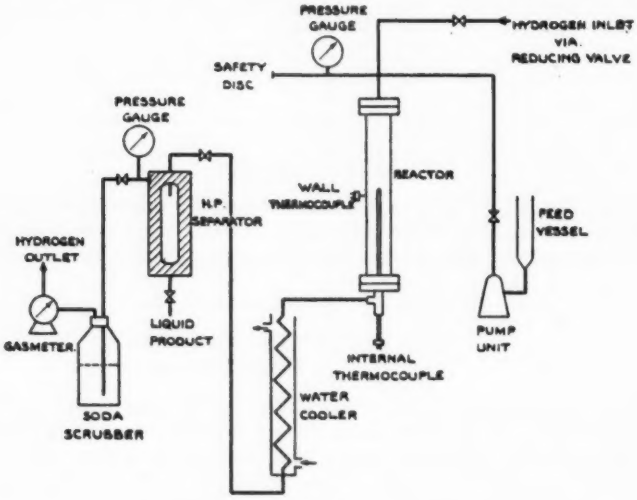


FIG. 5.

HYDROGENATION UNIT.

genation unit (Fig. 5) was designed and the running conditions to accomplish the production of material of nil B.N. from an average cracked gasoline ascertained. These conditions were found to be :—

Catalyst bed volume	400 ml
Catalyst bed temperature	435° F (224° C)
Catalyst	Nickel tungsten sulphide
Hydrogen pressure	250 p.s.i.g.
Hydrogen throughput	60 litres/hour
Space velocity	0·3 v/v/hr

To establish that the aromatic, naphthenic, and paraffinic hydrocarbons present would not be affected by such conditions, a straight-run naphtha (B.N. = nil) was processed under the same conditions. The hydrocarbon-type analysis of the product was determined according to the following procedure :—

(*a*) fractionation (25-plates, 40 : 1 reflux ratio) into cuts of specified boiling range;
(*b*) determination of individual aromatic hydrocarbons by ultra-violet spectroscopy in the cuts from (*a*) and summation to yield total aromatic content;
(*c*) de-aromatization by selective adsorption;
(*d*) fractionation (25-plates, 40 : 1 reflux ratio) of de-aromatized material from (*c*) into cuts of specified boiling range;
(*e*) estimation of naphthene and paraffin hydrocarbon content of cuts from (*d*) by specific refraction methods.

A similar hydrocarbon-type analysis was available of the original straight-

run naphtha. The T.B.P. curves of " hydrogenated " and original material before and after de-aromatization, shown in Figs. 6 and 7 are, within experi-

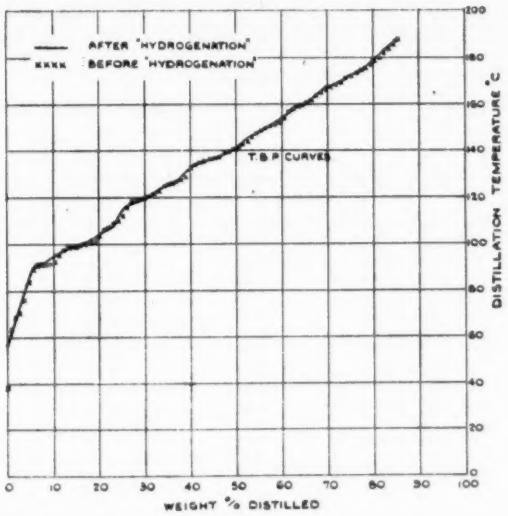

AFTER "HYDROGENATION"
BEFORE "HYDROGENATION"
T.B.P. CURVES
DISTILLATION TEMPERATURE °C
WEIGHT % DISTILLED
0 10 20 30 40 50 60 70 80 90 100
0 20 40 60 80 100 120 140 160 180 200

FIG. 6.

T.B.P. CURVES FOR STRAIGHT-RUN NAPHTHA BEFORE AND AFTER " HYDROGENATION."

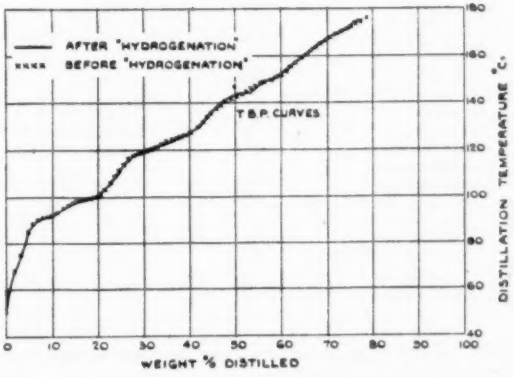

AFTER "HYDROGENATION"
BEFORE "HYDROGENATION"
T.B.P. CURVES
DISTILLATION TEMPERATURE °C.
WEIGHT % DISTILLED
0 10 20 30 40 50 60 70 80 90 100
40 60 80 100 120 140 160 180

FIG. 7.

T.B.P. CURVES FOR DEAROMATIZED STRAIGHT-RUN NAPHTHA BEFORE AND AFTER " HYDROGENATION."

mental error, identical. A comparison of the complete analyses is given in Table II. While the total aromatic-hydrocarbon contents show a slight decrease on hydrogenation there is no corresponding increase in

naphthene hydrocarbon contents, which would be expected if the aromatics were hydrogenating to naphthenes. The increase of paraffin contents, on the other hand, is due mainly to the desulphurization occurring (0·08 per cent wt to 0·002 per cent wt S), since cyclic compounds containing sulphur in the ring tend to dehydrogenate to non-cyclic hydrocarbons.

TABLE II.

Comparison of Hydrocarbon Type Composition of Original and "Hydrogenated" Naphtha.

Type.	Boiling range, °C.	Hydrogenated naphtha, wt %.	Original naphtha, wt %.	Difference hydrogenated–original, wt %.
Paraffins	I.B.P.– 68	1·34	1·05	+0·29
	68– 75	0·72	0·76	−0·04
	75– 85	0·38	0·36	+0·02
	85– 95	3·96	4·01	−0·05
	95–109	6·37	5·88	+0·49
	109–120	3·35	3·53	−0·18
	120–130	7·04	6·48	+0·56
	130–150	7·92	8·22	−0·30
	150–175	10·29	9·91	+0·38
	175–F.B.P.	8·96	9·18	−0·22
	I.B.P.–F.B.P.	50·33	49·38	+0·95
Naphthenes	I.B.P.– 68	0·24	0·20	+0·04
	68– 75	0·39	0·43	−0·04
	75– 85	0·94	1·02	−0·08
	85– 95	2·30	2·21	+0·09
	95–109	3·37	3·31	+0·08
	109–120	1·57	2·16	−0·59
	120–130	3·06	2·71	+0·35
	130–150	5·09	4·96	+0·13
	150–175	5·76	6·34	−0·56
	175–F.B.P.	9·77	8·98	+0·79
	I.B.P.–F.B.P.	32·51	32·32	+0·19
Aromatics	Benzene	0·43	0·48	−0·05
	Toluene	3·19	3·45	−0·26
	Ethylbenzene	1·01	1·36	−0·35
	*meta*Xylene	2·46	2·46	±0·00
	*para*Xylene	0·83	0·93	−0·10
	*ortho*Xylene	1·06	1·29	−0·23
	152 –160·8	1·28	1·25	+0·03
	160·8–175·2	3·00	3·13	−0·13
	175·2–F.B.P.	3·90	3·95	−0·05
	I.B.P.–F.B.P.	17·16	18·30	−1·14

The presence of sulphur compounds in the original straight-run naphtha would also tend to indicate higher aromatic contents when estimated by ultra-violet spectroscopy, due to a general overall adsorption throughout the range of wavelength employed in the method. The hydrogenation step, therefore, can be considered as satisfactory for the object in view, and the aromatic hydrocarbons, estimated in a product hydrogenated under the standard conditions, are equivalent to those present in the original material while the paraffins and naphthenes are also unchanged.

Determination of Aromatics.

The method of determining aromatics in a cracked gasoline, if the above controlled selective hydrogenation procedure is employed, is reduced to the simple case of determining the contents of such hydrocarbons in a straight-run product. The method of analysis preferred for aromatic content aims at the determination, as far as possible, of individual aromatic

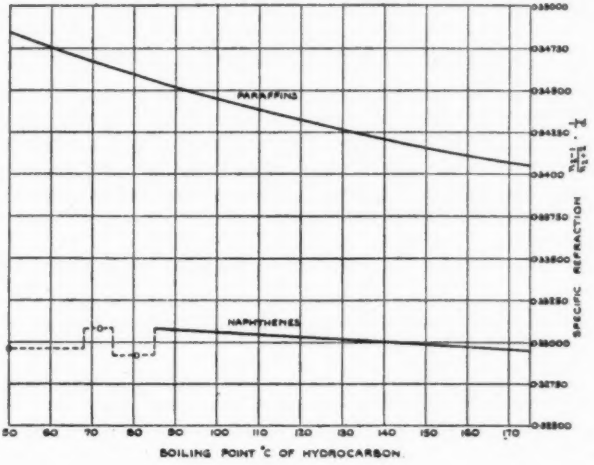


Fig. 8.

MEAN VALUES OF SPECIFIC REFRACTION FOR PARAFFIN AND NAPHTHENE HYDROCARBONS.

hydrocarbons, and comprises fractionation and ultra-violet spectroscopy. The hydrogenated material is fractionated into cuts of specified boiling ranges :—

(*a*) 45– 60° C.	(*d*) 120–126° C.	(*g*) 145–150° C.
(*b*) 60–117° C.	(*e*) 126–140° C.	(*h*) 150–160° C.
(*c*) 117–120° C.	(*f*) 140–145° C.	(*i*) 160–175° C.

Each of the above cuts is examined by ultra-violet spectroscopic methods [16] for individual aromatic hydrocarbons likely to be present from a consideration of boiling point, viz. : cut (*b*) benzene and toluene; cut (*e*) ethylbenzene *ortho-*, *meta-* and *para*xylene, etc. Experience has shown that cut (*a*) 45–60° C does not contain benzene, and examination of this cut can be omitted. In the case of cuts (*h*) 150–160° C and (*i*) 160–175° C the number of C_9H_{12} aromatic isomers does not permit at the present juncture complete estimation of individuals, and a total aromatic content only is obtained. From a knowledge of the yields of various cuts, the above individual aromatic contents furnish, on calculation, a detailed aromatic content of the hydrogenated cracked gasoline which can be taken to be identical with that of the original cracked gasoline. It must be pointed

out, however, that the actual yield of hydrogenated cracked gasoline represents $100 + x$ per cent of the cracked gasoline where x equals the percentage of hydrogen addition during the hydrogenation. For cracked gasolines of bromine number <40 the value of x is $<0{\cdot}5$ per cent. The determined contents of individual aromatic hydrocarbons, therefore, require multiplying by a factor to convert to true percentages of original cracked gasoline. The value of this factor lies between 1·000 and 1·005. For most practical purposes, this correction can be ignored.

Determination of Alkenes and Cyclenes.

The hydrogenated cracked gasoline may be freed from aromatic hydrocarbons by selective adsorption. The de-aromatized material can then be analysed for naphthene and paraffin content throughout the boiling range in a manner *identical* with that employed for the naphthene–paraffin components isolated as in Section 3. For reasons that are made obvious later, it is essential that the naphthene and paraffin analyses *are made in identical manner*.

The available data from the procedures outlined so far may be summarized thus :—

(*a*) naphthene and paraffin contents throughout the boiling range of the unsaturated and aromatic-free material;
(*b*) total aromatic content;
(*c*) naphthene and paraffin contents throughout the boiling range of the hydrogenated material.

On hydrogenation the non-cyclic olefins (alkenes) are converted to paraffins and cyclic olefins (cyclenes) to naphthenes; the analysis of the hydrogenated material therefore comprises the sums of the naphthenes and paraffins originally present plus those derived from the hydrogenation of the olefins. From the available data the cyclenes and alkenes originally present may be calculated as demonstrated below. The total yields of individual hydrocarbon types are first of all expressed as weight percentages of cracked gasoline sample.

Analysis of Cracked Gasoline before Hydrogenation.

	Per cent by wt.
Paraffins	p
Naphthenes	n
Aromatics + unsaturateds	$100-(p+n)$

Analysis of Cracked Gasoline after Hydrogenation.

Paraffins	p_1
Naphthenes	n_1
Aromatics	$100-(p_1+n_1)$

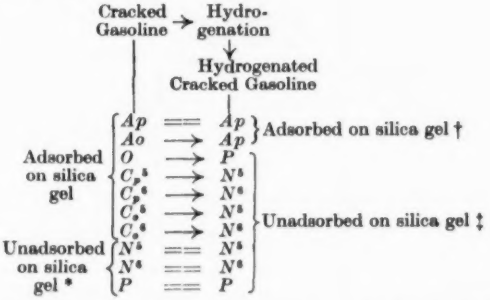
From these values the composition and concentrations of olefins in the cracked gasolines can be calculated from the equations :—

(*a*) Alkenes $= (p_1 - p)$ per cent by wt.
(*b*) Cyclenes $= (n_1 - n)$ per cent by wt.

The above relationships are equally true when applied to the bulk or any fraction of particular boiling range. The following schematic appreciation serves to indicate the various types of hydrocarbons assumed to be present

and the conversion or otherwise of these types during the processes and analyses described :

Let Ap = Aromatics with saturated side chains
Ao = Aromatics with unsaturated side chains
O = Alkenes
C_p^5 = Cyclenes—5-membered rings with saturated side chains
C_p^6 = Cyclenes—6-membered rings with saturated side chains
C_o^5 = Cyclenes—5-membered rings with unsaturated side chains or ring
C_o^6 = Cyclenes—6-membered rings with unsaturated side chains or ring
N^5 = Naphthenes—5-membered ring
N^6 = Naphthenes—6-membered ring
P = Paraffins



With the proviso that the fractionations of the naphthene–paraffin components of the cracked gasoline and of the hydrogenated product are performed in an identical manner, the contents of alkenes and cyclenes can be determined by the different equations quoted above.

Typical results of the intermediate analysis will be found in Table III, while the final calculated results are detailed in Table IV. In the interpretation of the final hydrocarbon-type composition, several points must be borne in mind :—

(*a*) First, aromatic hydrocarbons with unsaturated side chains, if such exist in cracked gasolines, are estimated as the corresponding aromatic hydrocarbons with saturated side chain, *e.g.*, vinyl benzene (styrene) would hydrogenate to ethylbenzene and be estimated as such. Members of this class of compounds are confined to the upper boiling range above 140° C, and the contents of the individual xylenes will not be affected, however, since no corresponding unsaturated compounds are possible. Results obtained by this method indicate low ethylbenzene contents, a fact which does not suggest undue proportions of styrene, and it is considered that, in general, the amounts of such unsaturated compounds are not large.

(*b*) Secondly, olefinic hydrocarbons are estimated as the corresponding saturated hydrocarbons. The non-cyclic olefins are estimated as paraffins. Each such paraffin can be derived, obviously, from several olefins, *e.g.*, *normal* heptane from heptenes, heptadienes, heptatrienes, heptynes, etc. For simplicity, only monolefins are named in Tables III and IV.

---

* Yield determined and analysed for naphthene content (n per cent) and paraffin content (p per cent) expressed as percentages by weight of cracked gasoline throughout the boiling range.

† Aromatics (a per cent) determined by U.V. spectroscopy, results expressed as percentages by weight of cracked gasoline.

‡ Analysed for naphthene content (n_1 per cent) and paraffin content (p_1 per cent) expressed as percentages by weight of cracked gasoline throughout the boiling range.

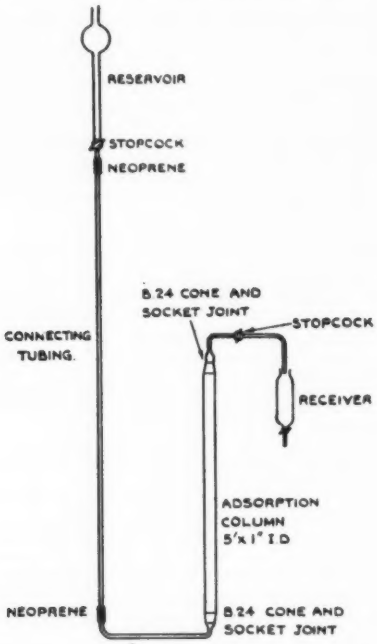


FIG. 9.
ADSORPTION COLUMN FOR HYDROGENATED CRACKED GASOLINE.

TABLE III.
Analysis of Cracked Gasoline.
Intermediate Naphthene-Paraffin Contents.

Boiling range, °C.	Naphthene + paraffin component of cracked gasoline.		Naphthene + paraffin component of hydrogenated cracked gasoline.		Cyclic olefins, wt % ($\Delta - \beta$).	Non-cyclic olefins, wt % ($\gamma - \alpha$).
	Naphthenes, wt % (β).	Paraffins, wt % (α).	Naphthenes, wt % (Δ).	Paraffins, wt % (γ).		
I.B.P.– 66	0·39	2·44	0·79	4·71	0·40	2·27
66– 70	0·82	5·68	1·28	7·88	0·46	2·20
70– 75	1·19	1·02	2·65	1·66	1·46	0·64
75– 85	0·92	0·16	1·74	0·37	0·82	0·21
85– 95	3·25	3·24	4·31	4·62	1·06	1·38
95–109	5·24	5·30	8·72	7·13	3·48	1·83
109–120	3·45	3·44	4·20	4·86	0·75	1·42
120–130	3·01	3·24	4·13	4·09	1·12	0·85
130–150	4·07	3·80	6·23	4·00	2·16	0·85
150–F.B.P.	3·24	3·08	8·26	3·18	5·02	0·10
Total	25·58	31·40	42·31	42·50	16·73	11·10

Note : All results are calculated on the basis cracked gasoline = 100 per cent.

TABLE IV.

Composition of Cracked Gasoline.

Hydrocarbon type.	Boiling range, °C.	Predominant hydrocarbons.	Wt, %.
Paraffin	45– 66	*iso*Hexanes	2·44
	66– 75	*normal* Hexane	6·70
	75– 85	Dimethylpentanes	0·16
	85– 95	Methylhexanes	3·24
	95–109	*normal* Heptane	5·30
	109–120	Methylheptanes and dimethylhexanes	3·44
	120–130	*normal* Octane	3·24
	130–150	*iso*- and *normal*-Nonanes	3·80
	150–175	*normal* Nonane and heavier	3·08
	Total		31·40
Naphthene	45– 66	*cyclo*Pentane	0·39
	66– 75	Methyl*cyclo*pentane	2·01
	75– 85	*cyclo*Hexane	0·92
	85– 95	Dimethyl*cyclo*pentanes	3·25
	95–109	Dimethyl*cyclo*pentanes and methyl*cyclo*hexane	5·24
	109–120	Dimethyl*cyclo*hexanes	3·45
	120–130	C_8 and C_9 ring octanaphthenes	3·01
	130–150	C_8 and C_9 ring nonanaphthenes	4·07
	150–175	Heavier	3·24
	Total		25·58
Non-cyclic olefins *	45– 66	*iso*Hexenes	2·27
	66– 75	*normal* Hexenes	2·84
	75– 85	Dimethylheptenes	0·21
	85– 95	Methylhexenes	1·38
	95–109	*normal* Heptenes	1·83
	109–120	*iso*Octenes	1·42
	120–130	*normal* Octenes	0·85
	130–150	*iso*- and *normal*-Nonenes	0·20
	150–175	*normal* Nonenes and heavier	0·10
	Total		11·10
Cyclic olefins *	45– 66	*cyclo*Pentenes	0·40
	66– 75	Methyl*cyclo*pentenes	1·92
	75– 85	*cyclo*Hexenes	0·82
	85– 95	Dimethyl*cyclo*pentenes	1·06
	95–109	Dimethyl*cyclo*pentenes and methyl*cyclo*hexenes	3·48
	109–120	Dimethyl*cyclo*hexenes	0·75
	120–130	C_8 and C_9 ring unsaturated octanaphthenes	1·12
	130–150	C_8 and C_9 ring unsaturated nonanaphthenes	2·16
	150–175	Heavier	5·02
	Total		16·73
Aromatics		Benzene	2·37
		Toluene	4·65
		Ethylbenzene	0·81
		*meta*Xylene	1·56
		*para*Xylene	0·58
		*ortho*Xylene	0·68
		Heavier	4·57
	Total		15·19

* The boiling ranges quoted are those of the corresponding saturated compound.

(c) Thirdly, cyclic olefins are estimated as the corresponding naphthenes. As in the case of the non-cyclic olefins, each such naphthene represents several unsaturateds, *e.g.*, methyl*cyclo*hexane can represent methyl*cyclo*hexenes, methyl*cyclo*hexadienes, methylene *cyclo*hexane, while higher cyclic olefins may be unsaturated with respect to ring and side chains. Only compounds of the methyl*cyclo*hexene type are quoted in Tables III and IV.

The above limitations are of particular significance in the analysis of materials produced under high-temperature–low-pressure conditions. The contents of both diolefins and aromatics with unsaturated side chains are much higher than in the case of gasolines from thermal or catalytic-cracking processes, and the results obtained must be accepted with due reserve.

The importance of method of analysis of cracked gasolines, yielding data as complete as that quoted in Table IV, is self evident.

Examples and Accuracy.

The proposed method has been applied to the analysis of a variety of hydrocarbon mixtures containing unsaturateds, and typical examples are given in Table V. Duplicate determinations of the hydrocarbon-type composition of an average cracked gasoline have indicated that the accuracies associated with the determination of the constituent hydrocarbons are :—

(a) Aromatic content—better than $\pm 0{\cdot}15$ per cent of sample whether concerned with bulk or individual content;
(b) Paraffin content—$\pm 0{\cdot}65$ per cent of sample for bulk content, better than $\pm 0{\cdot}4$ per cent of sample for narrow boiling range fractions;
(c) Naphthene—better than $\pm 0{\cdot}35$ per cent of sample whether concerned with bulk or narrow boiling range fractions;
(d) Alkene content—better than $\pm 0{\cdot}95$ per cent of sample whether concerned with bulk or narrow boiling range fractions;
(e) Cyclene content—better than $\pm 0{\cdot}75$ per cent of sample whether concerned with bulk or narrow boiling range fractions.

The accuracy of the method is dependent to a large extent on the efficiency of the fractional distillation, and the above assessment of errors is based on determinations using columns of twenty-five theoretical plates at 40 : 1 reflux ratio. Employment of higher fractionation efficiencies would minimise these errors, particularly with regard to the alkene and cyclene contents, since for the determination of these hydrocarbons a difference method is applied.

Time Schedule.

It will be appreciated that the proposed method cannot be considered as a substitute for any existing standard inspection procedure, since the data which it furnishes are obtained in detail. It is not surprising, therefore, that the time schedule is found to be somewhat lengthy, amounting to about 200 man-hr per sample. An approximation of the man-hours involved in the various sections of the method is :—

	Man-hr.
1. Adsorption and isolation of naphthene–paraffin component	12
2. Fractionation of naphthene–paraffin component	45
3. Hydrogenation of original sample	9
4. Fractionation of hydrogenated product	45
5. Determination of individual aromatic contents	8
6. Dearomatization of hydrogenated product	12
7. Fractionation of de-aromatized hydrogenated product	45
8. Analytical examination of fractions	8
9. Calculation	16
Total	200

TABLE V.

Typical Analyses—Cracked Gasolines.

Hydrocarbon type.	Boiling range, ° C.	Predominant hydrocarbons.	Gasoline A, wt %.	Gasoline, B, wt %.	Gasoline C, wt %.
Paraffin	45– 66	*iso*Hexanes	0·87	3·19	4·12
	66– 75	*normal* Hexane	5·04	6·41	0·73
	75– 85	Dimethylpentanes	0·17	0·28	2·10
	85– 95	Methylhexanes	1·25	2·92	
	95–109	*normal* Heptane	6·97	6·24	0·39
	109–120	Methylheptanes and dimethylhexanes	0·41	3·32	1·50
	120–130	*normal* Octane	8·65	3·58	
	130–150	*iso*- and *normal*-Nonanes	5·14	2·66	1·02
	150–175	*normal* Nonanes and heavier	8·77	2·86	
	Total		37·27	31·46	9·86
Naphthene	45– 66	*cyclo*Pentane	0·11	0·32	0·53
	66– 75	Methyl*cyclo*pentane	0·38	1·83	1·00
	75– 85	*cyclo*Hexane	0·43	1·22	1·66
	85– 95	Dimethyl*cyclo*pentanes	0·57	2·93	
	95–109	Dimethyl*cyclo*pentanes and methyl-*cyclo*hexane	1·40	5·65	1·73
	109–120	Dimethyl*cyclo*hexanes	0·26	2·10	1·42
	120–130	C_5 and C_6 ring octanaphthenes	1·08	3·80	
	130–150	C_5 and C_6 ring nonanaphthenes	1·66	4·44	1·54
	150–175	Heavier	2·69	3·75	
	Total		8·58	26·04	7·88
Non-cyclic olefins * (Alkenes)	45– 66	*iso*Hexenes	1·36	0·51	9·99
	66– 75	*normal* Hexenes	5·77	1·27	4·79
	75– 85	Dimethylpentenes	0·05	0·10	7·27
	85– 95	Methylhexenes	1·56	1·04	
	95–109	*normal* Heptenes	4·63	1·11	3·68
	109–120	*iso*Octenes	0·91	0·49	3·56
	120–130	*normal* Octenes	6·08	0·82	
	130–150	*iso*- and *normal*-Nonenes	4·78	1·74	5·13
	150–175	*normal* Nonenes and heavier	5·89	0·45	
	Total		31·03	7·53	34·42
Cyclic olefins * (Cyclenes)	45– 66	*cyclo*Pentenes	0·13	0·06	0·34
	66– 75	Methyl*cyclo*pentenes	0·72	1·07	2·47
	75– 85	*cyclo*Hexenes	0·33	0·48	2·16
	85– 95	Dimethyl*cyclo*pentenes	0·85	0·95	
	95–109	Dimethyl*cyclo*pentenes and methyl-*cyclo*hexenes	1·24	2·27	2·42
	109–120	Dimethyl*cyclo*hexenes	0·61	0·94	
	120–130	C_5 and C_6 ring unsaturated octanaphthenes	1·83	0·23	4·78
	130–150	C_5 and C_6 ring unsaturated nonanaphthenes	2·54	1·63	5·73
	150–175	Heavier	3·83	1·28	
	Total		12·08	8·91	17·90
Aromatics		Benzene	1·45	2·74	0·44
		Toluene	2·36	8·01	4·40
		Ethylbenzene	0·96	1·73	1·38
		*meta*Xylene	0·98	1·54	5·12
		*para*Xylene	0·39	3·65	2·56
		*ortho*Xylene	0·91	1·57	2·47
		Heavier	3·99	6·82	13·97
	Total		11·04	26·06	30·34

* The boiling ranges quoted are those of the corresponding saturated compound.

In conclusion the author desires to thank the chairman and directors of the Anglo-Iranian Oil Company Ltd. for permission to publish this paper, and to record his appreciation of the interest and criticisms of P. Docksey and J. W. Hyde of the Sunbury Research Station.

References.

[1] I.P. Standard Method I.P.–9/42. "Standard methods for testing petroleum and its products," 9th Edn., 1948.
[2] Francis, A. W. *Industr. Engng Chem.*, 1926, **18**, 821.
[3] Ormandy, W. R., and Craven, E. C. *J. Inst. Petrol. Techn.*, 1926, **12**, 68.
[4] Allen, C. C., and Duckwall, H. W. *Industr. Engng Chem. Anal.*, 1944, **16**, 558.
[5] Brame, J. S. S., and Hunter, T. G. *J. Inst. Petrol. Techn.*, 1927, **13**, 794.
[6] Hugel and Hibon. *Chim. et Ind.*, Spec. No. Feb. 1929.
[7] Danaila, Andrei, and Melinescu. *J. Soc. Chem. Ind.*, 1924, B857.
[8] Hoog, H., and Eichwald, E. *La. Soc. Chim. Néeil.*, 15.5.39, T58-5.
[9] Faragher, W. P., Morrell, and Levine. *Industr. Engng Chem. Anal.*, 1930, **2**, 18.
[10] I.P. Standard Method I.P.–3/42. (Ninth Edition 1948.)
[11] Kattwinkel. *Brennst. Chemie*, 8.22.353.
[12] Emergency Method of Test, A.S.T.M. Standards 1944, Part III, E.S. 45, pp. 1086–1099.
[13] Groennings, S. *Industr. Engng Chem. Anal.*, 1945, **17**, 361.
[14] Mair, B. J., and White, J. D. *Bur. Stand. J. Res.*, 1935, **15**, 51–62.
[15] Rossini, F. D., Mair, B. J., Forziati, A. F., Glasgow, A. R., and Willingham, C. B. *Proc. Amer. Petrol. Inst.*, 1942, **23** (3), 7.
[16] Gordon, R. R., and Powell, H. *J. Inst. Petrol.*, 1945, **31**, 28.
[17] Lecky and Ewell. *Industr. Engng Chem. Anal.*, 1940, **12**, 544.

OXIDATION OF TURBINE OILS IN THE LABORATORY.

By D. Wyllie and G. C. N. Cheesman.

Synopsis.

The behaviour of typical oils under oxidation test I.P. 114/47 has been observed both under the standard conditions and using a modified test. The possibility of substituting oxygen for air in this test is considered.

Peroxides are not present in more than negligible quantities during the oxidation of a conventionally refined turbine oil, but the peroxide value of the oil rises on the conclusion of the oxidation. This can be explained if the rate of peroxide decomposition is high compared with the rate of peroxide formation during high-temperature oxidation but not at room temperature, although the oxidized oil is susceptible to peroxide formation at room temperature.

The oxidation–corrosion test of Pope and Hall is not a suitable corrosion test for turbine oils, and the use of interfacial tension as a criterion of the extent of oxidation is not advised in view of the lack of correlation between interfacial tension and demulsification number.

Promising results were obtained when the behaviour of four pre-selective gear-box oils in oxidation test I.P. 114/47 was compared with service experience.

Introduction.

In connexion with the introduction of inhibited turbine oils into Naval Service the behaviour of typical oils under oxidation test I.P. 114/47 has been observed. Variations of the standard conditions have been made in order :—

(*a*) to get a better understanding of the course of reaction, and hence

(*b*) to develop a more rapid test procedure, and

(*c*) to collect information about the correlation of the oxidation test with the deterioration of oils in practice.

In this connexion the significance of peroxide value and interfacial tension is discussed. Some use has also been made of the test method devised by Pope and Hall.

Peroxide Values.

The importance of peroxidic compounds as intermediates in the oxidation of hydrocarbons has been demonstrated by among others George and Robertson [1] and Kreulen.[2] The presence of peroxide among the products of reaction was demonstrated by Larsen, Thorpe, and Armfield.[3] Williams [4] suggested that the determination of peroxide value could be used to indicate the course of deterioration of an oil in service.

A number of peroxide determinations have been carried out on turbine oils during the course of oxidation of these oils in this laboratory, and the significance of the results obtained is discussed.

The oxidation test methods employed have been :—

(a) *The oxidation–corrosion test of Pope and Hall*[5] *in which* 250 *ml of oil are maintained at* 100° *C in the presence of a steel test piece, round which a few turns of copper are wound* (0·12 *sq. cm. of steel surface per ml of oil and* 0·22 *sq. cm. of copper surface per ml of oil). The oil is contained in a special type of beaker fitted with a condenser, a stirrer, and an inlet tube through which moist oxygen is passed into the stirred oil at a rate of* 3 *litres per hour. Pope and Hall continue the oxidation until the interfacial tension falls below* 15 *dynes per cm.*

(b) *Oxidation test for turbine oil, I.P.* 114/47 *in which* 100 *g of oil are maintained at a temperature of* 110° *C for* 90 *hr in the presence of a metallic copper catalyst* (0·29 *sq. cm. per ml of oil). The oil is contained in a flask fitted with a condenser, and an inlet tube through which dry air is passed into the oil at a rate of* 2 *litres per hr.*

The oil used was a typical sample of Admiralty S.M.L.O., which is a conventionally refined, high V.I., uninhibited turbine oil. At intervals during the course of the reaction, approximately 1 g of oil was withdrawn for determination of peroxide value the method employed being that recommended by Stuffins and Weatherall.[6] The acid value, demulsification number, and the interfacial tension at an oil–distilled water interface were determined before and after oxidation. No appreciable concentration of peroxides was obtained during the oxidation of S.M.L.O. (see Table I), although marked oxidation did, in fact, take place. This type of oil was known to give peroxide values of at least 5 to 10 after prolonged service use, and the peroxide value of the laboratory oxidized oil was therefore redetermined after it had been standing in the laboratory for some days. It was then found that a marked increase in peroxide value had taken place.

In view of the fact that much of the published data on peroxide values relates to highly refined oils, a sample of water-white C.D. oil was submitted to the same oxidation processes and small samples were removed at intervals for the determination of peroxide value and acid value. In addition, the demulsification number of the oil was determined before and after oxidation.

Acid Value.

A modification of standard method I.P. 1/46A was employed to determine acid value on samples of the order of 1 g. The I.P. method consists essentially in taking up 10 g of oil in 100 ml of a mixture of 3 volumes of benzene and 2 volumes of alcohol, and titrating in the cold with $N/10$ caustic potash using alkali blue as indicator. This method works well with lightly coloured oils, but dark oils whose demulsification properties have deteriorated are more difficult to titrate. Substitution of carbon tetrachloride for benzene in the solvent mixture and use of a stoppered flask to allow of adequate shaking gives more satisfactory results with dark oils, since the high gravity of the carbon tetrachloride brings about more rapid separation of the emulsions formed. It was found that samples of the order of 1 g could be titrated if the volume of solvent mixture was reduced in proportion and a small stoppered bottle taken in lieu of a titration flask.

TABLE I.

TABLE I.

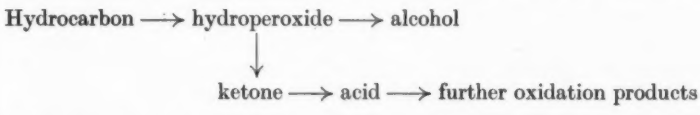
Development of Peroxides in a Conventionally Refined Turbine Oil.
(Admiralty S.M.L.O.)

Oxidation test.	Pope and Hall.		Modified Pope and Hall.		Modified Pope and Hall.		I.P. 114/47.		Modified I.P. 114/47.	
Temperature, °C :	100		100		100		110		110	
Air flow, l per hour :	3 (moist oxygen)		3 (moist oxygen)		3 (dry oxygen)		2 (dry air)		2 (dry air)	
Rate of stirring, r.p.m. :	850		850		850		Nil		Nil	
Catalyst :	Steel and copper		None		None		Copper		None	
Quantity of oil :	250 ml		250 ml		250 ml		100 g		100 g	
Peroxide value, ml 0·002*N* thiosulphate per g	Oxidation, hr	ml	Oxidation, hr	ml	Oxidation, hr	ml	Oxidation, hr	ml	Oxidation, hr	ml
	15	0·2	6	0·05	9	0·1	24	0·20	24	0·2
	23	0·2	24	0·2	19	0·5	42	0·15	42	0·2
	40	0·5	30	0·3	24	0·3	66	0·2	66	0·2
	48	0·2	38	Nil	42	0·3	90	—	90	—
	64	0·3	54	0·1	48	0·3	5 days' standing at room temperature	5·6	5 days' standing at room temperature	4·3
			72	0·2	72	0·05				
	20 days' standing at room temperature	2·3	12 days' standing at room temperature	6·7	90	0·1				
					12 days' standing at room temperature	5·1				
Acid value : Initial	0·06		0·06		0·06		0·06		0·06	
Final	0·36		0·10		0·11		0·70		0·08	
Demulsification number :										
Initial	215		215		215		215		215	
Final	1200 + (500 at 23 hr)		500		1200+		1200+		1200+	
Interfacial tension, dynes/cm :										
Initial	29·9 at 19° C		29·9 at 20° C		29·9 at 20° C		29·9 at 20° C		29·9 at 20° C	
Final	3·9 at 19° C (10·0 at 19° C at 23 hr)		24·1 at 19° C		19·5 at 20° C		27·4 at 19° C		20·5 at 19° C	

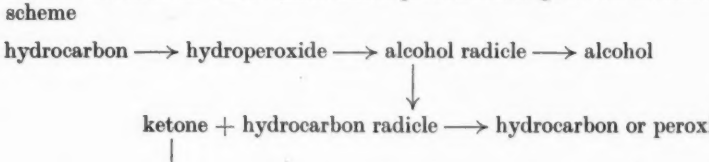
Use of very dilute caustic potash is not feasible, since excess water interferes with the end point and intensifies emulsion troubles. One operator working with $N/20$ caustic potash and a micro-burette can obtain excellent results if he adheres to the same conditions throughout and verifies his technique against results obtained with the standard method.

Discussion of Results.

George and Robertson [1] presented the following general picture for the course of oxidation of hydrocarbons when chain fission does not occur.



and for reactions in which chain fission predominates gave the alternative scheme


hydrocarbon ⟶ hydroperoxide ⟶ alcohol radicle ⟶ alcohol
ketone + hydrocarbon radicle ⟶ hydrocarbon or peroxide
acid ⟶ further oxidation products

For the present purpose these may be considered as consisting of two overall reactions or groups of reactions :—

(1) Production of peroxides from hydrocarbons or reaction products;
(2) Reaction of peroxides to give further reaction products.

The concentration of peroxides in the system at any given time will depend upon the relative rates of reactions (1) and (2). There is no *a priori* reason to suppose that a change in any of the conditions will affect equally peroxide formation and peroxide decomposition.

If the peroxides formed by S.M.L.O. are unstable under the conditions of oxidation and the decomposition reactions are considerably faster than the peroxide-forming reactions a negligible peroxide concentration could result.

It is known that this type of oil contains appreciable amounts of peroxides after it has been in service for some time, *e.g.*, a sample taken after twelve months' service at sea had acid value 0·25; demulsification number 1100; interfacial tension 21 dynes/cm at 16° C and a peroxide value of 5. Peroxide values of 2 to 7 were obtained on the oxidized oil after they had stood for some days in the cold. Therefore, it is reasonable to assume that when this type of oil has been oxidized peroxide formation occurs more readily in the cold than peroxide decomposition. Dornte [7] in 1936 reported that no appreciable amounts of peroxides were formed during the oxidation of the less highly refined oils and did not regard the peroxides as being of importance in the oxidation of these oils. The present writers consider that the absence of peroxides can be accounted for in the manner

already indicated and that this is in accord with the advance in the understanding of hydrocarbon oxidation which has taken place in the past twelve years.

The oxidation of C.D. oil (see Table II) followed the course which was to be expected with this class of oil,[2, 3, 7] *i.e.*, a marked rise in peroxide value and a rise in acid value in the presence of a catalyst. In the absence of a catalyst little change of any kind took place during the period of oxidation. The concentration of peroxides present in the oxidized oil from the Pope and Hall and I.P. 114/47 tests first rose on completion of the oxidation and then dropped to a steady but still considerable figure. It is considered that the unstable bodies present in the oil immediately after oxidation are sufficient to permit the peroxide-forming reactions to go forward faster than peroxide decomposition and that the steady state is reached when this initial momentum has been exhausted and the system has settled down. Bubbling air through the Pope and Hall sample in the cold produced a peroxide content a little different from that obtained by merely allowing the sample to stand undisturbed. The samples oxidized in the absence of catalysts contained no peroxides even after standing.

In the absence of sufficient data it is not proposed to discuss the reasons for the difference in behaviour of S.M.L.O. and C.D. oil, but attention is drawn to the paper by Larsen [3] in which the stability of lubricating oil is attributed to the content of natural inhibitors and to the work of Denison,[8] who demonstrated that sulphur-free lubricating oils form peroxides and that sulphur compounds rapidly reduce these peroxides.

Peroxide values obtained in the laboratory examination of used oils must clearly be interpreted in the light of the rest of the analytical data and the general character of the oil.

Interfacial Tension.

The surface tension at an oil–water interface is a fundamental measurement having considerable bearing on the emulsification of oil and water. The demulsification number of an oil is a practical measure of the stability of oil–water emulsions formed under standard conditions. Harkins and Zollmann [9] compared the interfacial tension and ease of emulsification of benzene–aqueous systems. Easy emulsification was obtained when the interfacial tension was reduced to less than 10 dynes/cm, and spontaneous emulsification was produced when the interfacial tension was reduced to less than 1 dyne/cm. The significance of the interfacial tension of lubricating oils was studied by Weiss and Vellinger,[10] who were able to correlate interfacial tension and degree of refinement of the oil as well as interfacial tension and extent of oxidation of an oil in the laboratory. Pope and Hall [5] laid down that their oxidation test should be continued until the tension at an oil–water interface dropped below 15 dynes/cm. This may be a satisfactory criterion of oxidation with uninhibited oils, and the results in column (2) of Table I suggest that the conditions of the Pope and Hall test may favour the production of low interfacial tensions.

Examination of turbine oils containing both oxidation and corrosion inhibitors revealed that the initial interfacial tension of a good oil of this class may be well below 15 dynes/cm. Oxidation of oils according to

TABLE II.

Development of Peroxide and Acids in C.D. Oil (Medicinal Paraffin).

Oxidation test.	Pope and Hall.			Modified Pope and Hall.			I.P. 114/47.			Modified I.P. 114/47.		
Temperature, °C:	100			100			110			110		
Air flow, l per hour:	3 (moist oxygen)			3 (dry oxygen)			2 (dry air)			2 (dry air)		
Rate of stirring, r.p.m.:	850			850			Nil			Nil		
Catalyst:	Steel and copper			None			Copper			None		
Quantity of oil:	250 ml			250 ml			100 g			100 g		
	Conditions	Peroxide value	Acid value	Conditions	Peroxide value	Acid value	Conditions	Peroxide value	Acid value	Conditions	Peroxide value	Acid value
	Initial	—	0·02	Initial	—	0·02	Initial	—	0·02	Initial	—	0·02
	5 hr Oxidation	Nil	0·03	7 hr Oxidation	0·6	0·05	6 hr Oxidation	1·9	0·06	4 hr Oxidation	Nil	0·03
	24 ,, ,,	5·2	0·06	19 ,, ,,	9·4	0·05	18 ,, ,,	24	0·09	12 ,, ,,	0·1	0·03
	34 ,, ,,	25	0·07	24 ,, ,,	Nil	0·06	30 ,, ,,	61	0·14	24 ,, ,,	0·2	0·04
	48 ,, ,,	55	0·45	43 ,, ,,	3·2	—	42 ,, ,,	51	0·24	30 ,, ,,	0·5	—
				54 ,, ,,	0·3	0·04	52 ,, ,,	85	0·39	36 ,, ,,	0·8	0·04
	3 days' standing at room temperature	90	0·44	66 ,, ,,	0·05	0·02	66 ,, ,,	83	—	48 ,, ,,	3·0	—
	5 days' do.	76	0·43							61 ,, ,,	5·1	0·03
	12 days' do.	75	—	3 days' standing at room temperature	0·2	—	3 days' standing at room temperature	112	0·77	73 ,, ,,	0·9	0·04
				5 days' do.	Nil	—	5 days' do.	103	—	84 ,, ,,	0·5	0·03
	3 days' standing +1 day bubbling air at room temperature	77	—	12 days' do.	0·3	—	12 days' do.	104	—	96 ,, ,,	0·2	0·02
	3 days' standing +2 days' bubbling air at room temperature	83	0·41	3 days' standing +1 day bubbling air at room temperature 6	0·1	—				3 days' standing at room temperature	0·2	—
										5 days' do.	Nil	—
										12 days' do.	Nil	—
Demulsification number:												
Initial	25			25			25			25		
After oxidation and 3 days' standing at room temperature	85			25			160			25		

method I.P. 114/47 will not necessarily have the same effect on interfacial tension as oxidation according to the method of Pope and Hall, but the results obtained when a selection of inhibited oils were oxidized according to method I.P. 114/47 are of considerable interest (see Table III). The two uninhibited oils shown in Table III do not give comparable changes.

TABLE III.

Comparison between Interfacial Tension and Demulsification Number.

Sample number.	Type of oil.	New oil.			Oil oxidized according to I.P. 114/47.		
		Interfacial tension at 20°C.	Demulsification number.	Acid value.	Interfacial tension at 20°C.	Demulsification number.	Acid value.
—	Conventionally refined turbine oil (Admiralty S.M.L.O.)	30	215	0·06	27	1200+	0·70
492 A/47	Solvent-refined turbine oil base stock	41	30	0·09	10	760	0·62
479 A/47	Solvent-refined oil plus oxidation and corrosion inhibitors	5	320	0·09	20	870	0·09
538 A/47	do.	13	200	0·10	17	400	0·15
900 A/47	do.	12	250	0·09	26	460	0·10
655 A/47	do.	15	200	0·10	13	490	0·21
656 A/47	do.	17	120	0·09	17	330	0·10
668 A/47	do.	32	185	0·09	28	440	0·08
721 A/47	do.	32	250	0·07	14	1200+	0·25
1701 A/47	do.	27	1200+	0·15	10	600	0·20

The inhibited oils can be divided into three groups.

(*a*) Oils having low demulsification numbers and low interfacial tensions which show some increase in demulsification number and a marked rise in interfacial tension after oxidation.* It is considered that in this class the inhibitors are responsible for the low interfacial tension and that partial destruction of the inhibitors without marked deterioration of the oil as a whole leads to the rise in interfacial tension;

(*b*) Oils having low demulsification numbers and moderately low interfacial tension which do not greatly change in either respect on oxidation;

(*c*) Oils having low demulsification numbers and high interfacial tension which exhibit a drop in interfacial tension after oxidation. The last oil in Table III is anomalous, the high initial demulsification number being caused by imperfectly dissolved inhibitor, *i.e.*, this is a case of emulsion stabilization by suspended solids.

Measurement of interfacial tension may in all cases give a true indication of the ease with which emulsions may be formed, but it clearly does not indicate the stability of such emulsions. This is probably dependent upon the mechanical properties of the interfacial film.

THE OXIDATION–CORROSION TEST OF POPE AND HALL.

No detailed study of this test has been made but the following information has been obtained so far.

* Although low figures on new inhibited oils are not uncommon, a large increase in interfacial tension is not a frequent occurrence.

(1) Measurement of interfacial tension is not a satisfactory criterion of oxidation if this test is to be used with inhibited oils. Measurement of demulsification number in lieu of interfacial tension would be much more satisfactory in practice. Interfacial tensions can more usefully be determined in fundamental investigations than routine analysis.

(2) No noticeable corrosion was observed even in presence of C.D. oil. The test is therefore not suitable for use as a corrosion test with oils likely to be used in present-day turbines.

(3) No theoretical objection can be seen to the use of this test as an oxidation test when the extent of the oxidation reaction is followed by measurement of acid value and demulsification number.

(4) There are certain practical difficulties in the operation of this apparatus in that the hooks on which the test pieces are suspended are very readily broken off and the special pads which fit over the top of the beakers are liable to become detached from their mountings. Furthermore, the apparatus has to be specially constructed; a serious drawback these days.

Oxidation Test for Turbine Oil I.P. 114/47.

This test method was devised by a panel of the Lubricating Oil Pool Technical Committee and it was found that a dividing line could be drawn between uninhibited oils and inhibited oils of the quality of U.S. Navy Turbine Lubricating Oil, Symbol 2190T. Satisfactory inhibited oils had acid values of less than 0·2 and demulsification numbers of less than 1200 after oxidation. The duration of this test is 90 hr, and although very much shorter than some of the test methods which have been discussed in the literature [11, 12] it would be of considerable advantage if an even shorter test period could be devised. With this end in view six typical turbine oils have been examined by the standard method. Some have also been oxidized (*a*) in the absence of catalyst and (*b*) substituting oxygen for air (see Tables IV and V).

Table IV.

The Behaviour of Typical Turbine Oils in Oxidation Test I.P. 114/47.

Reference number:	1.	2.	3.	4.	5.	6.
Type of oil:	Admiralty S.M.L.O. (conventionally refined oil).	Solvent-refined proprietary oil.	Oil 2 plus oxidation inhibitor.	U.S. Navy 2190T oil. (Contains oxidation and corrosion inhibitors.)	Proprietary oils uninhibited but other details unknown.	
Acid value:						
Before oxidation	0·06	0·06	0·06	0·06	0·08	0·11
After "	0·52	0·45	0·09	0·08	0·41	1·10
Viscosity at 100°F:						
Before oxidation	65·7	71·0	69·2	90·7	67·3	77·7
Viscosity ratio: Oxidized / Unoxidized at 100°F	1·08	1·02	1·03	1·01	1·04	1·08
Viscosity index:						
Before oxidation	112	98	100	105	108	97
After "	108	102	100	105	104	104
Demulsification number:						
Before oxidation	220	80	105	240	240	160
After "	1200+	900	500	130	1200+	1200+

TABLE V.

Effect of (a) *Removing the Catalyst and* (b) *Substituting Oxygen for Air in Oxidation Test I.P.* 114/47.

Reference number of oil (compare Table IV):		1.	2.	4.	5.	6.
Increase in acid value during oxidation.						
Air plus catalyst	90 hr	0·46	0·39	0·02	0·33	0·99
Air alone	90 ,,	0·04	0·01	—	−0·04	−0·01
Oxygen plus catalyst	18 ,,	0·49	—	—	—	—
	24 ,,	—	0·28	Nil	—	0·33
	30 ,,	1·06	—	—	—	0·48
Increase in demulsification number.						
Air plus catalyst	90 hr	1200+	820	−110	1200+	1200+
Air alone	90 ,,	160	220	—	1200+	1200+
Oxygen plus catalyst	18 ,,	1200+	—	—	—	—
	24 ,,	—	970	−50	—	1200+
	30 ,,	1200+	—	—	—	1200+
Viscosity ratio: $\frac{\text{oxidized oil at } 100°F.}{\text{unoxidized oil at } 100°F.}$						
Air plus catalyst	90 hr	1·08	1·02	1·01	1·04	1·08
Air alone	90 ,,	1·05	1·04	—	1·02	1·02
Oxygen plus catalyst	18 ,,	1·07	—	—	—	—
	24 ,,	—	1·01	1·01	—	1·05
	30 ,,	1·10	—	—	—	1·05
Change in viscosity index.						
Air plus catalyst	90 hr	−4	+4	Nil	−4	+7
Air alone	90 ,,	−5	−5	—	−9	−3

Broadly speaking two main types of end products in the oxidation of lubricating oils have been reported: (*a*) acids, alcohols, and soaps; and (*b*) condensation and polymerization products such as "neutral resins" and asphalts. After oxidation, acids are measured directly, but soaps, resins, and asphalts are, in the test in question, detected indirectly by their deleterious action on the demulsification properties of the oil. The presence of polymerization products will frequently be revealed by a drop in the V.I. of high V.I. oils. Attempts to separate asphalts using standard method I.P. 6/45 do not normally yield any results when applied to oxidized turbine oils, doubtless owing to the relatively low degree of polymerization of the so-called asphaltenes.

All the oils chosen for examination had high V.I., and would according to Fenske [13] be expected to yield acids rather than condensation products on oxidation. The degree of refining of the oils did, however, vary considerably, and two of the oils contained oxidation inhibitors.

Under the standard test conditions oils 1, 2, and 5, and in particular oil 6 showed marked increase in acidity, the inhibited oils, 3 and 4, showing little change. Three of the oils (1, 5, and 6) gave demulsification numbers of 1200+ after oxidation, but the changes in viscosity and V.I. of these oils, although small, are sufficient to show that the extent of the polymerization and condensation reactions is not the same in all cases. It is apparent that oil 2 contained only a relatively small percentage of condensation products after oxidation, since its demulsification number was still less than 1200 and its V.I. increased slightly. The two inhibited oils show little changes of any description, the drop in demulsification number of the 2190T oil is probably connected with destruction of the inhibitors.

Oxidation of four of the oils in the absence of catalyst demonstrated the difference between oils 1, 2, 5, and 6. As was anticipated no appreciable change in acid value occurred in any instance, but the tendency of oils 5

and 6 to undergo polymerization and condensation was demonstrated by the breakdown of their demulsification properties. The change in V.I. of oils 1 and 2 demonstrated that the same type of reaction must have begun, but it did not proceed far enough to bring about any marked change in their demulsification properties.

The oxidation tests in which oxygen was substituted for air can be interpreted in the light of the foregoing. It is clear that oil 1 can be oxidized to approximately the same extent as occurs under the standard conditions by only 18 hr treatment with oxygen. Oil 2, relatively stable against condensation and polymerization, but susceptible to acidity formation, was not attacked in 24 hr of oxygen treatment to the same extent as it was under the standard conditions. Oil 6, however, lost its demulsification properties in 24 hr in spite of the fact that even after 30 hr its acid value was less than half what it had been under the standard conditions. In this case the acids are probably undergoing further reactions and not accumulating rapidly as was the case when air was employed in the oxidation. The inhibited 2190T oil was practically unaffected in 24 hr.

It is clear that substitution of oxygen for air will reduce the duration of the test from 90 hr to 20 to 30 hr, but that different oils are not affected to the same extent. More detailed study of the products and also the mechanism of the oxidation is required before the relative action of air and oxygen can be assessed.

Correlation of the Standard Test Method with Service Experience.

As was stated above, the conditions were laid down to provide a comparison between oxidation of inhibited and uninhibited oils. No complete comparison between experience in the field and laboratory results can be hoped for in the near future, but Wilford's [14] work on the lubrication of pre-selective gear-boxes offered an opportunity for comparison between laboratory experiments and service conditions similar to those obtaining in turbine gears. Four samples supplied by Wilford for this purpose have been given a single oxidation test each. The results obtained are shown in Table VI, together with a brief note on the oils' performance in gear-boxes and Wilford's reference numbers.

It is gratifying to find that the test rated the acid values of the oxidized oils in the same order as service experience. The demulsification numbers of the oils after oxidation do not give the same order of merit. This is perhaps not surprising, since the acid value and not the demulsification number of the oils would be the most important factor in a gear-box, whereas demulsification number becomes of major importance in a ship. The demulsification numbers do correlate with the changes in viscosity and V.I. of the oils. It is of interest to note that the very stable oil N never generated any concentration of peroxides, and that the other three oils all have low or negligible peroxide values rising somewhat after the oxidation process.

Conclusions.

1. Under the conditions of oxidation obtaining in a typical laboratory test procedure a conventionally refined turbine oil yields only negligible

TABLE VI.

Comparison between Results Given by Oxidation Test I.P. 114/47 and Experience in Pre-selective Gear-boxes.

Wilford's reference letter: Performance in gear-boxes:	N. *Outstandingly successful.* White oil with -naphthol as oxidation inhibitor.			R (inhibited). *Satisfactory.* Oil R with amine type oxidation inhibitor			R. *Unsatisfactory.*			Not mentioned. Inhibited turbine oil. *Better than* R *but not satisfactory.*		
	New	Oxidized		New	Oxidized		New	Oxidized		New	Oxidized	
Appearance:	Colourless	Yellow green-brown sludge		Yellow	Brown		Yellow	Dark brown		Yellow	Brown	
Viscosity: at 210° F, cs	7·94	—		8·33	8·48		8·97	9·07		7·01	7·22	
,, 100° F, cs	68·0	—		64·3	66·5		67·7	68·2		56·1	61·4	
Viscosity index	88	—		107	106		114	115		87	80	
Demulsification number	60	500		1050	1200+		150	1200+		180	1200+	
Saponification value	0·6	0·6		0·6	0·8		0·6	2·0		0·0	1·7	
Acid value	0·06	18 hr Oxidation	0·06	0·04	18 hr Oxidation	0·06	0·02	18 hr Oxidation	0·12	0·04	18 hr Oxidation	0·09
		42 ,, ,,	0·07		42 ,, ,,	0·07		70 ,, ,,	0·50		70 ,, ,,	0·26
		66 ,, ,,	0·09		66 ,, ,,	0·10		90 ,, ,,	0·72		90 ,, ,,	0·34
		90 ,, ,,	0·08		90 ,, ,,	0·19						
Peroxide value	0·8	18 hr Oxidation	0·5	0·4	18 hr Oxidation	0·2	1·5	18 hr Oxidation	1·3	0·8	18 hr Oxidation	0·7
		42 ,, ,,	0·2		42 ,, ,,	Nil		70 ,, ,,	1·9		70 ,, ,,	0·9
		66 ,, ,,	0·2		66 ,, ,,	0·3		90 ,, ,,	2·3		90 ,, ,,	1·4
		90 ,, ,,	0·3		90 ,, ,,	1·3						
		1 day later	0·1		1 day later	1·5		3 days later	3·3		3 days later	2·4
		3 ,,	0·2		3 ,,	4·2		7 ,,	4·7		7 ,,	6·0
		14 ,,	0·4		14 ,,	5·1						

peroxide values while the oxidation is in process, but a marked rise in peroxide value takes place on the conclusion of the high-temperature oxidation. This can be explained by the assumption that peroxide formation and peroxide destruction take place at different relative rates during and after the oxidation.

2. Interfacial tension may correlate with ease of demulsification, but is not a substitute for demulsification number.

3. The oxidation–corrosion test devised by Pope and Hall is not a suitable corrosion test for turbine oils, and the use of interfacial tension as a measure of oxidation is not advised. No extensive use of this method has been made.

4. The effect of varying the conditions of I.P. 114/47 are discussed, and the possibility of shortening the duration of the test by using oxygen instead of air is considered.

5. Oxidation of four pre-selective gear-box oils under the conditions of I.P. 114/47 gave reasonable correlation between laboratory results and service experience.

ACKNOWLEDGMENT.

The authors desire to give thanks to the Chief of the Royal Naval Scientific Service for permission to publish this paper and to Dr C. D. Lawrence for valued encouragement and advice.

Admiralty Chemical Department,
H.M. Dockyard,
Portsmouth.

References.

[1] George, P., and Robertson, A. *J. Inst. Petrol.*, 1946, **32**, 382, 400.
[2] Kreulen, D. J. W. *J. Inst. Petrol.*, 1946, **32**, 515, 525, 656.
[3] Larsen, R. G., Thorpe, R. E., and Armfield, F. A. *Industr. Engng Chem.*, 1942, **34**, 183.
[4] Williams, K. A. *Analyst*, 1945, **70**, 409.
[5] Pope, C. L., and Hall, D. A. *Petroleum*, 1943, **6**, 168.
[6] Stuffins, —, and Weatherall —. *Analyst*, 1945, **70**, 403.
[7] Dornte, R. W., *et al. Industr. Engng Chem.*, 1936, **28**, 26, 863, 1342.
[8] Denison, G. H. *Industr. Engng Chem.*, 1944, **36**, 477.
[9] Harkins, —, and Zollmann, —. *J. Amer. Chem. Soc.*, 1926, **48**, 69.
[10] Weiss, H., and Vellinger, E. "Science of Petroleum," *Proc. World Petrol. Congr.*, 1934, **2**, 423.
[11] Smith, C. N., and Snyder, G. H. S. *J. Inst. Petrol.*, 1946, **32**, 313.
[12] Auld, S. J. M., and Lawrie, C. *Trans. Inst. Marine Engrs*, 1946, **58**, 125.
[13] Fenske, M. R., *et al. Industr. Engng Chem.*, 1941, **33**, 516.
[14] Wilford, A. T. *J. Inst. Petrol.*, 1907, **33**, 1.